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AEC RESEARCH AND DEVELOPMENT REPORT

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Serial No.: A-3630
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CLINTON ENGINEERING WORKS

CARBIDE AND CARBON CHEMICALS CORPORATION

LABORATORY DIVISION

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STANDARD METHOD OF ANALYSIS FOR K-25

J. L. Gabbard
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INVENTORY

PLANT RECORDS DEPT.
CENTRAL FILES

INV.
REC. 17331
B-21796

FILE
X-REF.
X-REF.

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INERTNESS OF C-816 OR C-716 TO C-616

Certain impurities in C-716 and C-816 react with C-616 forming a non-volatile residue. The ratio of the weight of this residue to the weight of the original sample of C-716 or C-816 expressed in percent is a measure of the reactivity (inertness) of the C-716 or C-816 with C-616.

I. Apparatus

A. Construction

All equipment must be constructed of glass, D-29, copper, brass, nickel or monel. Metals must be properly conditioned to render their surfaces inert to C-616. (See "Conditioning of Equipment"). Metal joints must be made by silver soldering or by metal welding. All valves used are 3/8 inch Kerotest valves of packless construction with copper impregnated D-29 seats.

Apparatus consists of:

1. Nickel or Monel reactors of 120 to 150 ml. capacity fitted with detachable valves and flare connections (See Figure 1).

2. A good vacuum system with a mechanical pump and a mercury diffusion pump capable of evacuting the entire system to one micron. This system is constructed of glass. (To the right of valve G in Figure 2.)

A C-616 charging system attached to the vacuum system constructed so that approximately the same amount of C-616 can be pipetted into a number of reactors. This system consists of a vessel in which C-616 is stored, a pipet cylinder, and connections for the reactors. (To the left of valve G in Figure 2).

3. Equipment for heating valves and lines and for heating and freezing reactors.

4. An oven to give a uniform heat of 100°C.

5. A mass balance capable of weighing to 2 kg. with an accuracy of 0.5 mg.

B. Cleaning Apparatus

All metallic apparatus to be used with C-616 must be cleaned and conditioned so as to render it inert to C-616. Lines and reactors which have been used with C-616 must be cleaned and reconditioned periodically.

1. Cleaning of new reactors and lines:

   (a) IN THE HOOD, clean the lines or reactors thoroughly with a mixture of 60 ml. of nitric acid and 40 ml. of sulfuric acid.

   (b) Wash thoroughly with distilled water and dry in the oven at 100° C.

2. Reactors that have accumulated more than 1 gram of residue must be cleaned.

   (a) IN THE HOOD, remove the valve from the reactor and rinse thoroughly with hot water.

   (b) Rinse with about 50 ml. of boiling saturated ammonium oxalate solution.

   (c) Rinse thoroughly with hot water.

   (d) Put the solutions from the first two rinsings in the designated container.

(e) Rinse well with acetone and dry at $100^{\circ}C$. overnight.

(f) Take the valve apart, clean and dry in a similar manner.

(g) Before assembling, check for mechanical defects and re-place the seat if necessary.

(h) Reassemble the valve and reactor.

(i) Charge the reactor with 80 lb. per sq. in. gage of G-74 and immerse in water. If a leak is observed, correct and test for leak again.

3. Cleaning of C-616 charging line:

The C-616 charging line should be cleaned from time to time as dust accumulates in the line.

(a) Disconnect the line at valves C & G and move to the hood.

(b) Plug the manifold connections and clean the line with water and ammonium oxalate in the manner outlined for reactors.

(c) Take the valves apart and clean and dry in a similar manner.

(d) Before assembling valves, check for mechanical defects and replace seats if necessary.

(e) Evacuate the line and heat with a torch (or electric heater) to dry.

(f) Reassemble the line, pressure to 80 lb. per sq. in. gage with G-74 and test for leaks with soap and water.

Note: Fome time to time the ballast tank may require cleaning in the same manner.

C. Conditioning of Apparatus

After cleaning, all apparatus, whether new or used must be conditioned.
ALL CONDITIONING OPERATIONS MUST BE CARRIED OUT IN THE HOOD.

1. Charge the apparatus with 15-20 lbs. per sq. in gage of 100% C-216 and allow to stand for 24 hours at 100°C.

2. Allow the conditioned apparatus to cool and discharge the C-216.

3. Pressure several times with dry G-74 and discharge. (For a more complete discussion of conditioning, see the procedure on "C-616 Conditioning".

D. Care of Apparatus

1. Care of Reactors

The operator should keep in mind that the analysis is a quantitative one in which results will be appreciably affected should the reactor or reactor valve change in weight during the operation from any source other than the normal gain from reaction residue. With this in mind, the operator should be careful not to lay reactors down where foreign matter will adhere to them, should not bang them against other objects, should take the utmost care not to allow wrenches to slip on them while putting on or removing from the line and should see that threaded connections are in good condition so that threads will not be stripped from valves,

2. Care of Traps

(a) Use only Trap S for discharging reactors. Empty C-616 from no more than 10 reactors into this trap. In discharging the mixture of C-816 and C-616 from reactors it may be necessary to switch the discharge into trap L by turning stop-cock 5 when trap S becomes full, Use Trap L for only the minimum time required to install and

evacuate a clean trap in the S position. Immediately switch back to the S trap.

(b) Never permit the L-28 level in the dewar around the trap to get below the level of the condensed material in the trap.

(c) When traps containing C-616 are removed from the line, quickly transfer them to the hood and fill with an excess of water to stop the evolution of HF and to halt the etching of the glass. Designated containers are provided for waste C-616 and C-816.

E. The McLeod Gage (See Figure 4)

1. Construction

The McLeond Gage is made of a 100-200 ml. flask, B, into which is sealed a capillary, Cap. 1, which is closed at the upper end. This capillary should be 1 mm. or less inside diameter. The lower end of B is sealed to a vertical tube, T, leading to a mercury well, M. Sealed to this tube at A is a side-arm tube of the same diameter as tube T and leading through cock G to the main line of the vacuum system. Sealed into this side-arm at two places is a capillary, Cap. 2, of the same diameter as Cap. 1. Attached to the side-arm of the mercury well is a three-way stopcock, D, one arm of which is a fine capillary, Tip 1. The remaining arm of this cock, D, is attached to a vacuum pump, the purpose of which is to lower the mercury from the gage after a reading without breaking the vacuum. Attached behind the two capillaries is a scale consisting of two portions; namely, scale

x which shows the compression ratio (v/V) of the trapped gas formerly occupied by B, and scale y which shows the pressure in centimeters or millimeters on the gas trapped in Cap. 1.

2. Operation

When a reading is desired

(a) Slowly turn cock D so that the atmosphere enters through the fine tip and forces the mercury up Tube T into the capillaries. The rush of mercury into the capillaries should be controlled by use of the finger over the capillary Tip 1; thus reducing the chances of breaking Cap. 1.

(b) Allow the mercury to rise as high as possible into Cap. 1, still keeping the mercury in Cap. 2 on scale y.

3. Reading and Calculation

(a) Theoretical

Pressure in the system at the time the reading is taken is calculated by using Boyle's Law: $P/p = v/V$ where P = unknown; p = pressure of trapped gas in Cap. 1 which is the difference in the height of mercury in the two capillaries and is read on scale y; v = the volume of trapped air in Cap. 1 and V = the total volume of bulb B.

(b) Practical

Due to the fact that scale y on the McLeon Gages starts at the top of Cap. 1, the distance from this point to the line on scale x indicating the compression ratio values 10^{-5}, 5×10^{-5}, 10^{-4} and 5×10^{-4} and having the respective values of 0.2 cm., 1 cm., 2 cm., and 10 cm. must be

added to the y scale reading in order to give the pressure in cm. of mercury. The reading on the FC line are actually made by stopping the top of the mercury column in Cap. 1 on the highest division of scale x that can be used keeping the top of the mercury column in Cap. 2 on scale y. Calculations are then simplified as follows:

Position of Mercury of Cap. 1	Pressure of system in microns
10^{-5}	$\dfrac{0.2 \text{ cm.} \neq \text{cm. as shown on scale y}}{10}$
5×10^{-5}	$\dfrac{1.0 \text{ cm.} \neq \text{cm. as shown on scale y}}{2}$
10^{-4}	2.0 cm. $\neq$ cm. as shown on scale y
5×10^{-4}	5 (10 cm. $\neq$ cm. as shown on scale y)

4. Lowering mercury into well after reading McLeod Gage.

   (a) Start vacuum pump attached to Cock D.

   (b) Turn cock D to open line from vacuum pump into mercury well. When mercury has all been lowered into the well M, close cock D.

5. Precautions

   (a) Never read the McLeod Gage unless you are sure that no C-616 is in the line. C-616 reacts with mercury and will cause it to stick in the capillary.

   (b) Differential Pressure Problems

      (1) In order to lower the pressure on the gage from atmospheric by means of the two vacuum pumps, cocks D and G must be opened very slowly and at the same time.

·(2) If cock D or G must be regreased, pressure differ-
ences must always be taken into consideration before
removing either stopcock.

II. Procedure

A. Operation of Vacuum System

Refer to Figure 2. Consider the vacuum system as all of the diagram
to the right of valve G. It is completely constructed of glass with
the exception of the flexible copper tubing section.

1. Assume the system to be at atmospheric pressure, valve G closed,
and all stopcocks but 3 open, the three traps clean with prop-
erly greased ground glass joints held in place by rubber bands,
and all stopcocks properly greased. All ground joints must be
lubricated with Apiezon M stopcock grease. Raise dewar flasks
around the three traps and fill with L-28.

2. Start the mechanical pump.

3. Turn the variac controlling the mercury pump heater on and set
it at 60 volts.

4. Turn the condenser jacket water on.

5. The system is now being evacuated with the exception of Trap S
or Trap L depending upon which way stopcock 4 is open. Some
time is required for the mercury pump to begin operating but
pressures down to a few microns can usually be obtained in a
few minutes. As soon as the mechanical pump has obtained a
"fair" vacuum it will assume a quiet operation.

6. McLeod gage readings can be taken now to check the pressure in
the system. Turn stopcock 3 to the position at which it admits

atmosphere to the flask above the mercury of the gage. Control
the mercury rise in the gage by partially constricting the pass-
age for atmosphere with the finger tip. The mercury should rise
slowly in the bulb and into the capillary section in front of
the calibrated porcelain plate. Accurate readings can now be
obtained in the lower pressure range (.01 micron) - See Section
I, part E on McLeod Gage.

7. Open stopcock 3 to the vacuum pump which removes the atmosphere
from the mercury well and returns the mercury to the flask.

8. Turn stopcock 3 to the off position and close stopcock 2 if
there is any possibility that the system is to be opened to
higher pressures. Never open stopcock 2 to the line when the
gage is in an evacuated condition unless the mechanical pump
is running quietly signifying the system is also in an evacuated
condition. When conditions are proper to take a McLeod gage
reading, stopcock 2 should be opened approximately 1 minute in
advance of starting the reading operation.

9. Within an hour the mercury pump should be in full operation and
the system ready for service. Read the McLeod gage until a
pressure of less than 5 microns (preferably 1 micron) is obtained.
Should desired pressure not be obtained after a reasonable time
the cause can usually be traced to small leaks at one or more of
the glass joints. A leak can ordinarily be readily isolated
and remedied. There is a possibility of a leak through valve G,
a crack in the glassware or inefficient operation of the pumps,
but it is wise to check the glass joints first. If necessary
isolate and correct the leak.

B. Operation of C-616 Charging System

Refer to Figure 2. Consider the C-616 charging system as that part of the diagram to the left of valve G. The purpose of this system is to deliver a constant amount of C-616 from the storage cylinder into reactors attached to the manifold.

1. Filling the Pipet

(a) Assume the vacuum system is evacuated, the charging system is at atmospheric pressure with G-74, and valves A, B, E, F, and G are closed.

(b) Make sure that stopcock 2 of the vacuum system is closed.

(c) Slowly open valve G. The hand on the pressure gage will immediately start to drop from 0 toward the 20 inches of Hg reading and the mechanical pump will be heard operating loudly. About one half hour may be required to evacuate this section since the volume of the pipet or ballast tank is rather large.

(d) After pumping on this section for a few minutes, the pressure gage will read near 28 inches and the pump will have resumed quiet operation. Open stopcock 2 and read the McLeod gage. When a reading of less than 5 microns (preferably 1 micron) is obtained, close valves G and C. The charging system is now ready to pipet C-616.

(e) Open valve E and allow C-616 as a gas at its vapor pressure at room temperature to fill the ballast tank. $3\frac{1}{2}$ to 4 inches rise in pressure will deliver 8 grams ($\pm$ 3 grams)

to the ballast tank. When the pressure has risen this amount, close valve E.

2. Evacuating the Reactors

The charging system is now ready to deliver C-616 to the reactors.

Proceed as follows:

(a) Place the reactors on the line connections using D-29 gaskets as shown in Figure B. These gaskets insure leak-tight connection without undue strain on threads.

(b) Without opening reactor valves open valves G, A, and B and pump a vacuum of less than 5 microns over the reactors.

(c) Open the reactor valves slowly, one at a time; evacuate to less than 5 microns (preferably 1 micron).

(d) Close valve G.

3. Charging Reactors

(a) Close valve B. Raise a bucket containing L-28 around the first reactor on the top branch of the line and hold in place for about one minute.

(b) Open valve C allowing the C-616 to distill over into the frozen reactor. The pressure gage returns to about 28 inches reading.

(c) Close valve C and open valve E. Allow $3\frac{1}{2}$ to 4 inches pressure of C-616 to enter the ballast tank. Close valve E.

(d) Close the valve on the reactor just charged and move the L-28 bucket to the next reactor in line.

-12-

    (e) Open valve C and repeat the procedure for each of the reactors.

4. Removing C-616 from Lines

    (a) Raise dewars of L-28 around traps S, L, and A.

    (b) With valves on the reactors, valves E and F and stopcock 4 closed, open stopcock 5 into the S trap and slowly open valve G. Immediately the traces of C-616 in the lines and the ballast tank will begin to distill over into trap S.

    (c) Heat all the metal lines and tanks being discharged of C-616 to 60°C. and maintain at this temperature. Allow to drain into trap S for 5 minutes. Also warm reactors to approximately room temperature with torch.

    (d) Open stopcock 5 into trap L, and allow lines to drain for an additional minute.

    (e) Open stopcock 4 and pump on the system for 2 minutes (The auxilliary cold trap A will catch any traces of C-616 that might get through trap L).

    (f) Close valves G and D.

    (g) Admit about 1 atmosphere of G-74 through valve F and remove the reactors.

    (h) Place the reactors in the oven at 100°C for $3\frac{1}{2}$ hours.

C. Discharging C-616 From Reactors

    1. Remove reactors from the oven and allow to cool to room temperature.

1.1

-14-

their valves thus retaining the vacuum, and remove from the line.

(b) Rinse a clean filter pour tube as shown in Figure 3 with 2 or 3 cc. of the sample (placing rinsings in designated waste bottle) and attach the tube to the reactor.

(c) Pour 56 cc. of C-816 into the pour tube from a graduate (also rinsed).

(d) Open the reactor valve slowly in order to admit the sample to the reactor with a minimum of air.

(e) Close reactor valve.

(f) Weigh the reactors on a triple beam balance to 0.5 gram. 56 cc. of C-816 should weigh very near 100 g.

(g) Place the filled reactors on the line and obtain a maximum 5 micron vacuum over the valves.

(h) Place L-28 buckets around all reactors and freeze for a minimum period of 10 minutes.

(i) Open reactor valves and pump a maximum 5 micron vacuum on the reactors.

(j) Charge reactors with C-616 as you charged the empty reactors; exceptions as follows:

    (1) Keep all reactors in L-28 baths.

    (2) Keep all reactor valves closed while charging except the one being charged.

    (3) Keep all valves and connections warm so that the C-616 will go into the one open reactor.

    (4) Place in the oven for 24 hours plus 1 hour lag time.

2. Discharging the Reactors

    (a) Remove the reactors from the oven and treat similarly to

         the blank reactors; exceptions as follows:

         (1) Give more care to performing a controlled distilla-

              tion. This can be done by raising the temperature

              slowly to 100°C. by the variac control and by having

              a minimum distillation time of 1 hour.

         (2) Handle emptied reactors in the same manner as the

              blank reactors and weigh to 0.5 mg.

III. Calculation of Results:

$$\frac{(\text{Final weight} - \text{initial weight}) \times 100}{\text{Weight of 816 in reactor}} = \% \text{ non-volatile residue}$$

1.1

D-29 GASKET FITS HERE

VALVE FITTED ONTO
ANNEALED COPPER SEAT
IN FLARE NUT

SCALE- 1" = 1"

FRONT VIEW

RT. SIDE VIEW
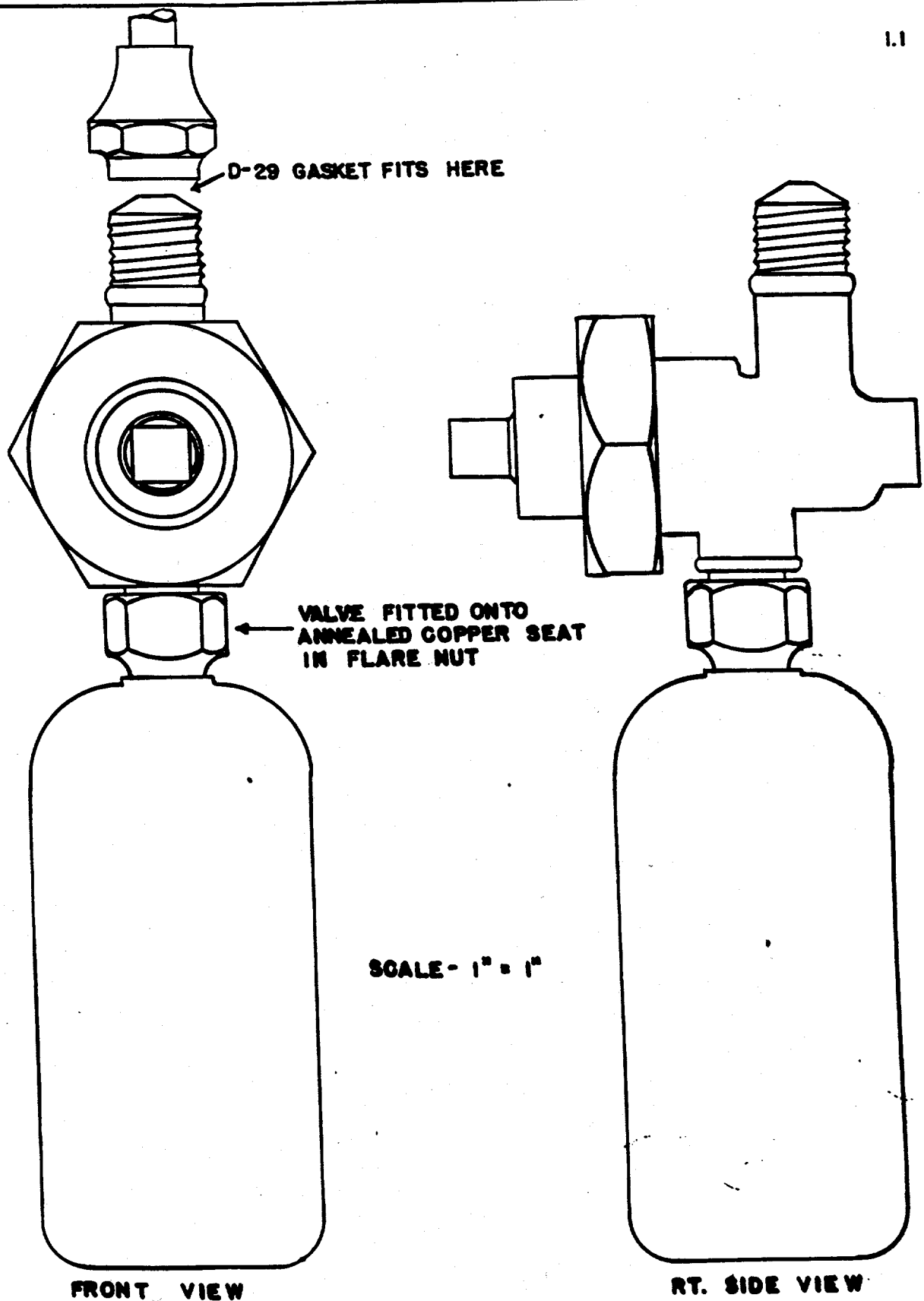
FIGURE 1
NICKEL REACTOR
WITH
3/8" KEROTEST VALVE

FIGURE 2

VACUUM SYSTEM & 616 CHARGING SYSTEM
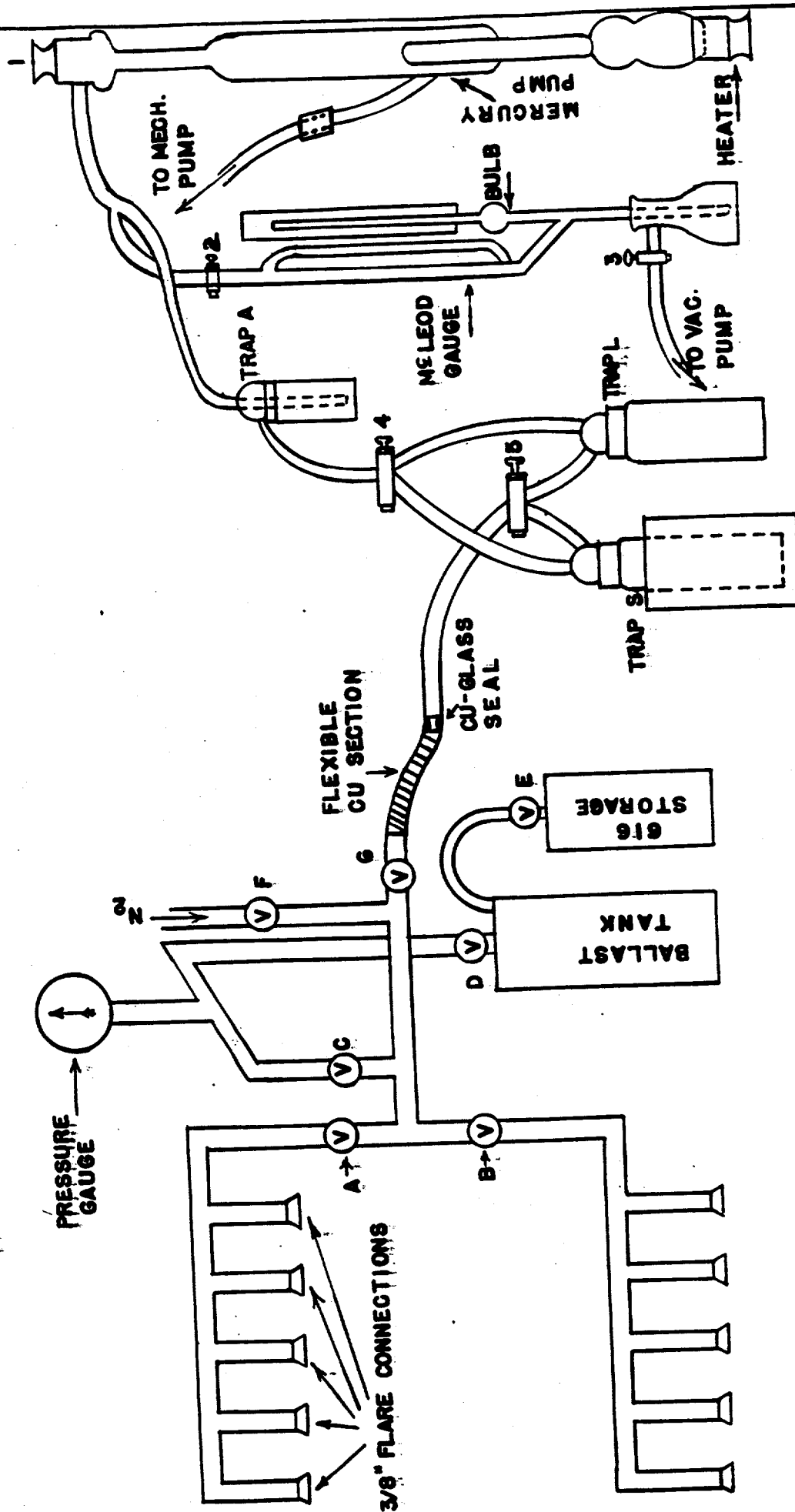
FIGURE 3

FILTER POUR TUBE
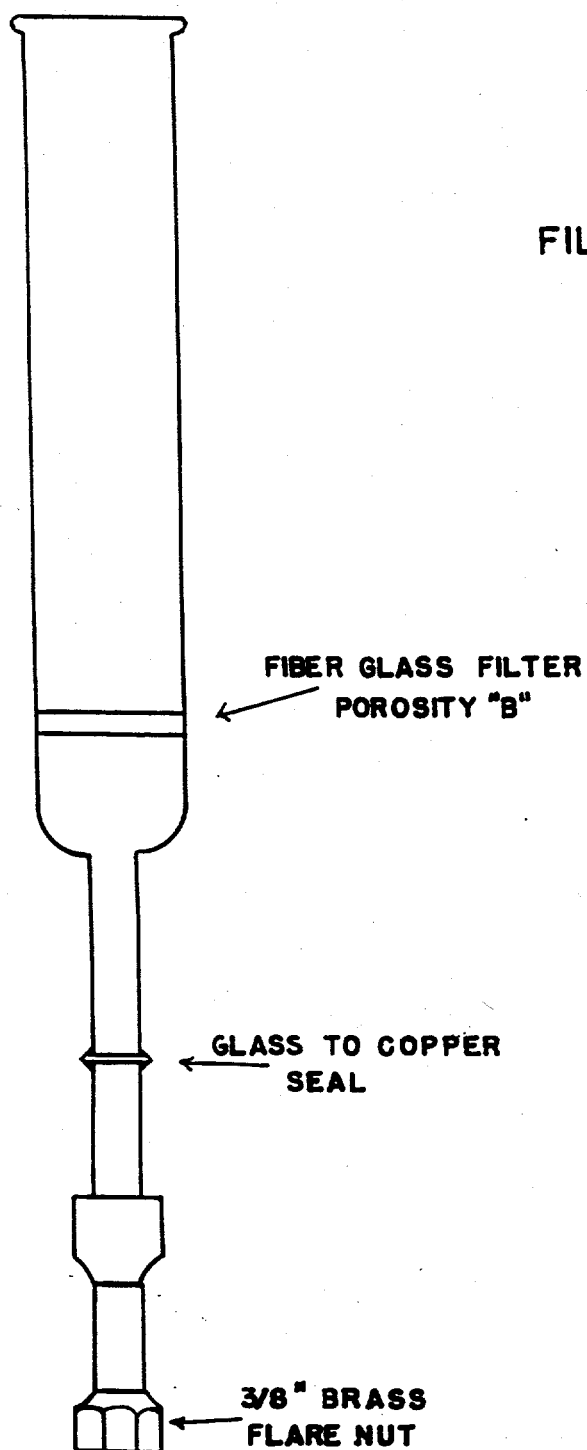
K-416 GASKETS
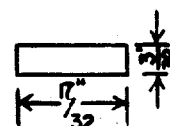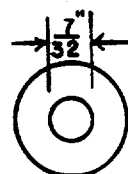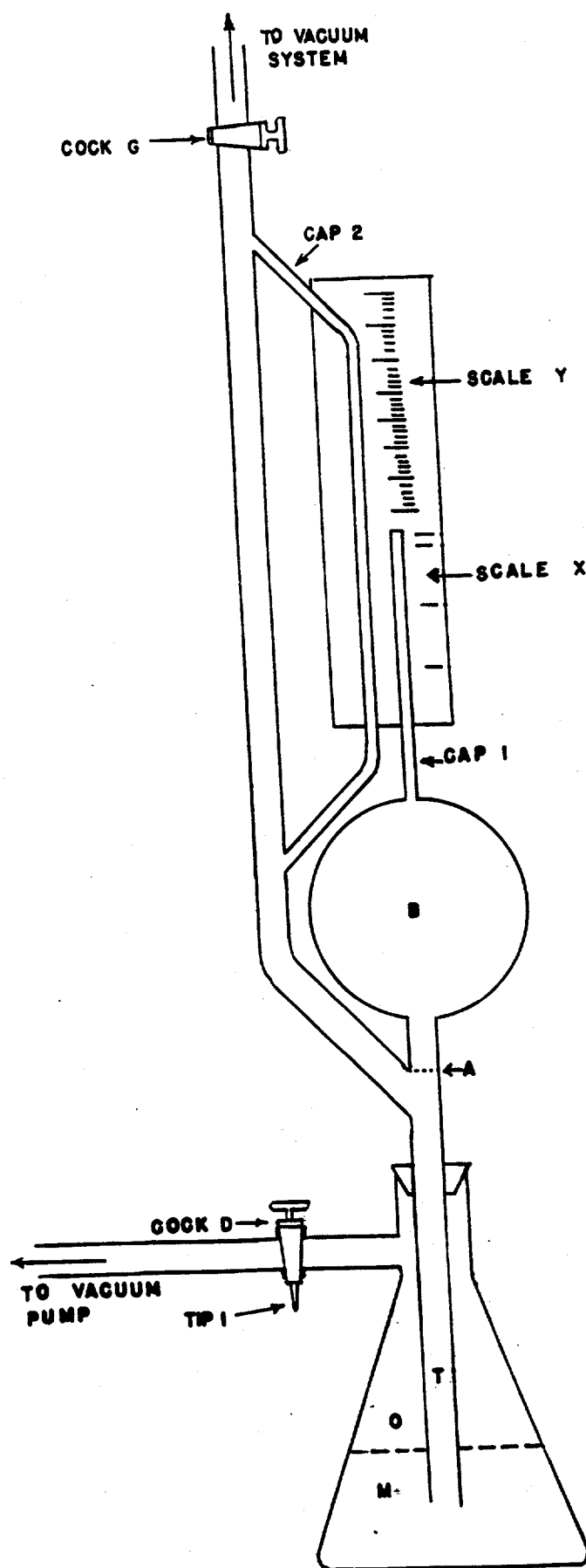
FIBER GLASS FILTER
POROSITY "B"

GLASS TO COPPER
SEAL

3/8" BRASS
FLARE NUT

TO VACUUM
SYSTEM

COCK G

CAP 2

FIGURE 4

THE McLEOD GAGE

SCALE Y

SCALE X

CAP 1

B

A

COCK D

TO VACUUM
PUMP   TIP 1

T

O

M

CHARGING SYSTEM

TRAP S

PRESSURE
GAUGE

NICHROME
RESISTANCE
WIRE

F

G

C

D

E

REACTORS

-616
STORAGE
TANK

BALLAST

REACTOR HEATERS

CONFIDENTIAL

PRESSURE GAUGE

MERCURY PUMP

HEATER

TRAP A

McLEOD GAUGE

MECH. PUMP

TRAP L

O VAC PUMP

VACUUM SYSTEM

FLEXIBLE CU SECTION

TRAP S

THERMOS
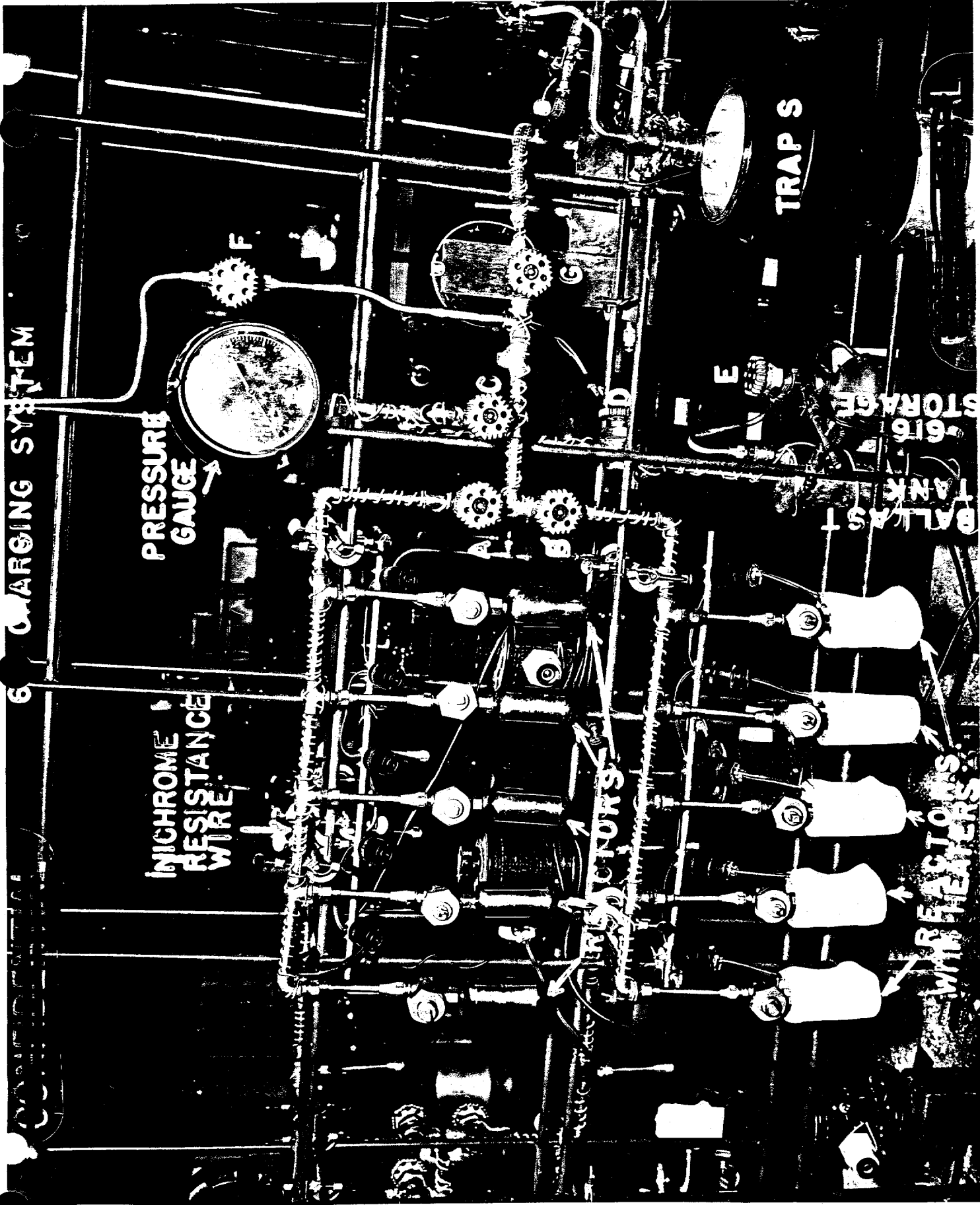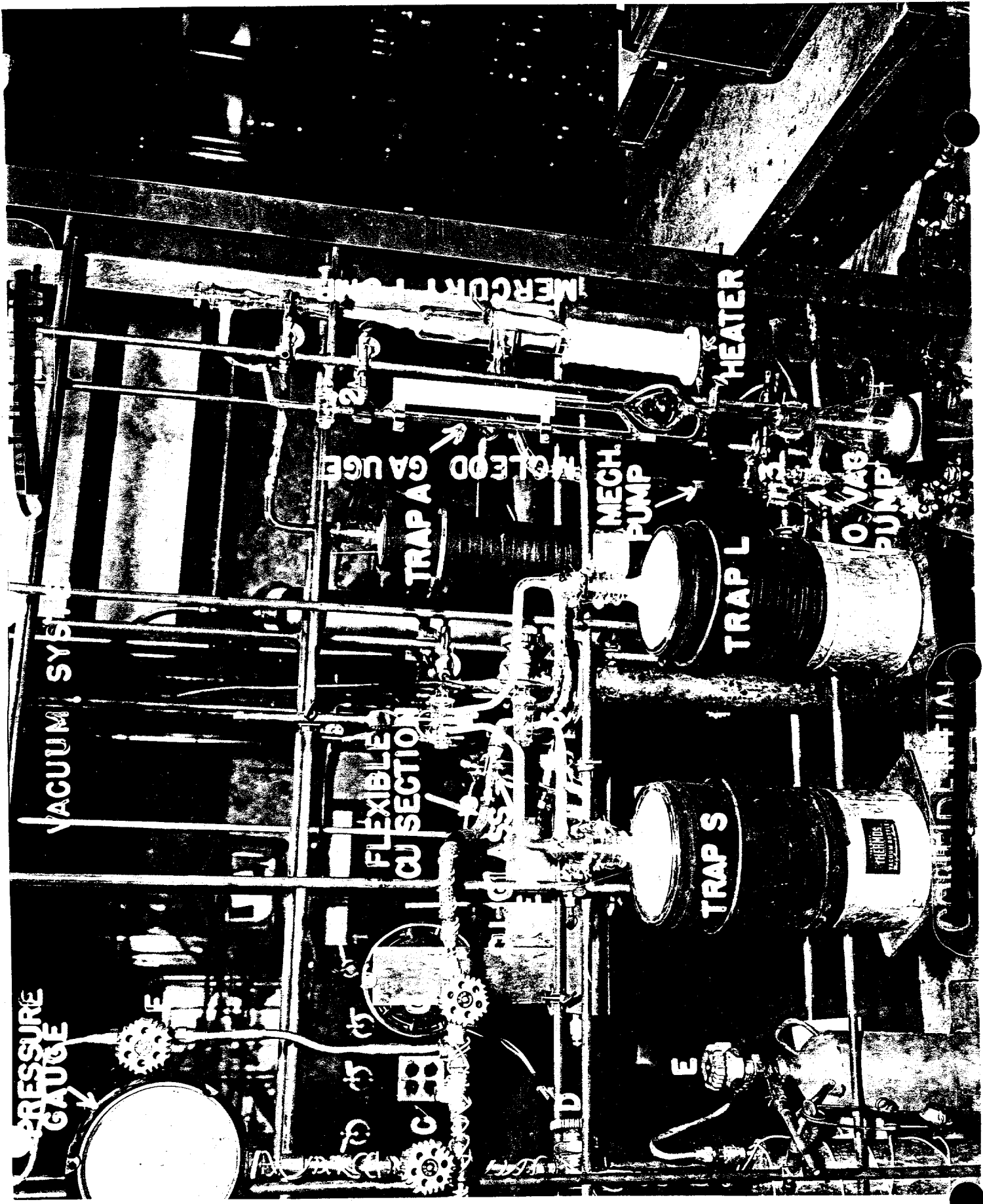
INERTNESS OF C-2144 AND MFL LUBE OILS TO C-616

When C-616 is heated with C-2144 or MFL, certain impurities in the oil reduce the C-616 to form TF_4. The relation between the weight of TF_4 formed and the total weight of oil used, expressed as per cent, is taken as a measure of the reactivity (inertness) of the lube oil with C-616.

I. Apparatus

1. The vacuum system and C-616 charging system are shown in Figure 2, "Inertness of C-816 and C-716 to C-616".

2. Glass reactors shown in Figure 1.

3. Any standard analytical titrimeter using oxidation - reduction electrode system.

4. Protective tube made from 1-1/4 inch copper tubing and shown in Figure 2.

II. Reagents

A. Preparation

1. Ceric Ammonium Sulfate (0.05 N)--Weigh out two 300 gram portions of ceric ammonium sulfate and put each in a 4 l. beaker. Add 500 ml. of concentrated sulfuric acid to each beaker. VERY SLOWLY add 500 ml. of water to each beaker WITH CONSTANT STIRRING. Add four more 500 ml. portions of water to each beaker being careful to avoid spattering. The total volume in each beaker will now be approximately 3 l.

In an 18 l. carboy measure 10 l. of distilled water and add the contents of each beaker to the carboy. Rinse each beaker with 1 l. of distilled water bringing the volume in the carboy to 18 l. Mix the contents of the carboy thoroughly.

2. Ceric Ammonium Sulfate (0.01 N) - Carefully measure 200 ml. of the 0.05 N ceric ammonium sulfate solution into a 1 l. volumetric flask. Add 45 ml. of concentrated sulfuric acid and dilute to the mark with distilled water.

3. Ferrous Ammonium Sulfate (0.05 N) - Weigh out 180 g. $FeSO_4(NH_4)_2SO_4$. $6H_2O$ and put in a 4 l. beaker. Add 2.5 l. of distilled water and then slowly with stirring add 500 ml. of concentrated sulfuric acid. Measure 5 l. of distilled water into a 9 l. carboy and add the 3 l. of solution to it. Rinse out the beaker with distilled water to make volume up to 9 l. Mix thoroughly.

4. Ferrous Ammonium Sulfate (0.01 N) - Dilute 200 ml. of the above 0.05 N ferrous ammonium sulfate to 1 l. with distilled water.

B. Standardization

1. Ceric Ammonium Sulfate (0.01 N) -

    (a) Dry approximately 5 grams of primary standard grade sodium oxalate in a 100° C. oven for at least two hours.

    (b) Weigh accurately between 0.1 and 0.2 grams sodium oxalate into a 250 ml. volumetric flask. Dissolve in distilled water and dilute to volume.

    (c) Pipette accurately 25 ml. sodium oxalate solution into a 600 ml. beaker containing approximately 140 ml. of distilled water and 20 ml. of 18 N H_2SO_4.

    (d) Heat the solution to 80° C. and titrate electrometrically with the ceric ammonium sulfate solution using the Beckman

pH meter (Calomel-Platinum Electrode System). If the
solution is allowed to fall below 80° C. the end point is
very sluggish.

(e). Calculation

$$N = \frac{\text{gms. of sodium oxalate}}{\text{ml. of solution x .067}}$$

2. Standardization of Ferrous Ammonium Sulfate (0.01 N) -

(a) Since ferrous ammonium sulfate solution is unstable it is
necessary to determine the ratio of ceric ammonium sulfate
to ferrous ammonium sulfate daily.

(b) Pipette accurately 25 ml. of 0.01 N ceric ammonium sulfate
into a 600 ml. beaker containing approximately 140 ml. of
distilled water and 20 ml. of 18 N H_2SO_4.

(c) Bring the solution to 90° C. $\angle 10^{\circ}$ C. and titrate electro-
metrically with 0.01 N ferrous ammonium sulfate, using the
Beckman pH meter (Calomel-Platinum Electrode System).

(d) Calculation

$$R = \frac{\text{ml. ceric ammonium sulfate}}{\text{ml. ferrous ammonium sulfate}}$$

III. Procedure

A. Filling the Reactor:

1. Weigh the clean, dry (see "Cleaning Apparatus", Sect. I-B,
"Inertness of C-816 or C-716 to C-616") reactor empty on a
triple beam balance to 0.1 gram.

2. Load the reactor with 10 to 15 ml. of the sample with a long-stemmed funnel avoiding, if possible, getting sample on the walls of the reactor neck. This operation is greatly facilitated by having the sample and the funnel heated to about 75° C.

3. Weigh the loaded reactor to the nearest 0.1 gram.

B. Charging the Reactor with C-616

1. Place the reactor on the vacuum line, using two neoprene gaskets in the flare. Do not tighten with a wrench.

2. Raise a dewar containing L-28 around the reactor.

3. When the oil has frozen solid, evacuate the system to a pressure of 5 microns or less.

4. Charge the reactor with C-616 in a manner similar to the method used in charging the metal reactor in determining the inertness of C-816.

5. With 5-11 g. of C-616 condensed in the reactor over the oil sample, seal off the stem slowly and uniformly with a torch about half way between the reactor top and the flare nut.

NOTE: Operate the vacuum system and the charging system exactly as described in "Inertness of C-816 or C-716 to C-616". For best results, charge only two reactors at a time. A C-616 pressure of 3-1/2 to 4 inches Hg will give the desired (5-11 g.) in each reactor.

C. Heating the Reactor:

1. Allow the reactor to warm to approximately room temperature.

2. Place it in the protective tube and heat in the 100° C. oven for three hours plus a lag time of 40 minutes.

3. At the end of three hours forty minutes, remove the reactor from the oven and place in a trichlorethylene-dry ice bath (or any bath cold enough to quickly condense the C-616). It is best to have the reactor and material cold enough to condense the C-616 but not cold enough to freeze the MFL or C-2144 solid.

D. Unloading the Reactor:

1. In the hood, wearing protective gloves, behind a safety shield, holding the reactor with test tube tongs, heat the reactor about one inch from the tip in a gas flame until it is red. Be sure the reactor tip is dry before placing it in the flame and be careful to see that the reactor inclines away from the flame.

2. Invert the reactor and simultaneously immerse the hot tip into a 400-600 ml. beaker containing 100 ml. of distilled water and 20 ml. of concentrated sulfuric acid. The reactor stem will break off or crack sufficiently that firm pressure against the bottom of the beaker will break it off allowing solution to rise into the reactor.

3. Shake the contents of the reactor into the beaker and rinse three times with 10 ml. portions of distilled water.

E. Preparation for Titration:

1. Add 50 ml. of the 0.01 N ceric sulfate solution and stir. If the solution remains green in color, add 25 ml. portions of ceric sulfate until the solution is slightly yellow.

2. Place on the hot plate and boil gently for 15 minutes. Boil longer if necessary. All the green solid should dissolve, giving a slightly yellow solution. If the solid is slowly soluble, add 20 ml. of 18 N sulfuric acid (do not add concentrated acid to a boiling solution) and continue to boil gently until solution is complete. If the solution changes from a yellow to a green color, add 25 ml. portions of 0.01 N ceric sulfate until the color is again yellow.

F. Titration:

1. Connect the calomel and platinum electrodes for measuring oxidation-reduction potentials to the Beckman pH meter and adjust the instrument according to the instructions attached to the lid.

2. Place beaker containing solution from (E) on hot plate and heat to $90° \not< 10°$ C. This temperature should be maintained throughout the titration.

3. Lower the electrode system (Fig. 2) into the beaker.

4. The e.m.f. of the calomel-platinum electrode system in the hot solution, containing an excess of ceric ammonium sulfate, should be at least 1050 mv. An e.m.f. value less than 1050 mv. may be increased by one or both of the following operations:

   (a) Add 20 ml. of 18 N sulfuric acid (an excess of acid is necessary for a good titration).

   (b) Add 25 ml. of 0.01 N ceric ammonium sulfate solution. (An excess of this reagent is obviously necessary).

5. Titration Procedure

    (a) Add ferrous ammonium sulfate from the burette, slowly but steadily, with good stirring until the e.m.f. change resulting from the addition of a 0.5 ml. portion of reagent is large (10 mv.).

    (b) Add 2-3 drops portions, recording the total value of reagent added and the e.m.f. values, until the e.m.f. drops approximately 700 mv.

    (c) Add 0.5 ml. portions, recording total volume of reagent added and e.m.f. values, until the e.m.f. change with a 0.5 ml. portion of reagent is less than 10 mv.

6. Plot the ml. of reagent vs. the e.m.f. The end point is where there is a maximum change of e.m.f. per unit of reagent added (See Figure 3).

G. Cleaning and Care of Electrodes:

Clean electrodes, essential for a good titration are assured by the following procedure:

1. Platinum electrode

    (a) At the end of a series of titrations (during a series of titration if the electrodes become sluggish) wash the electrodes twice in 5 ml. portions of Freon in a test tube.

    (b) Place the electrode in hot (125° C.) c.p. cleaning solution and allow to cool and stand in this solution until it is to be used for further titrations.

(c) Rinse the electrode, just before using, with copious amounts of tap water followed by distilled water.

2. Calomel Electrode

(a) At the end of a series of measurements (during the measurements if the electrode system becomes sluggish) thoroughly clean the electrode with a cloth saturated with Freon. Follow this operation with a cloth saturated with distilled water.

(b) Rinse the electrode well with distilled water, place the rubber tip on the electrode and allow to stand in distilled water until it is to be used for further titrations.

(c) In case the saturated KCl solution becomes contaminated, flush out the electrode thoroughly with distilled water, saturated KCl solution, and refill with saturated KCl solution.

IV. Calculations:

$$\% \text{ residue} = \frac{[\text{ml. } Ce(SO_4)_2 - (\text{ml. } FeSO_4)(R)] (N_{Ce(SO_4)_2}) (15.7)}{\text{wt. oil sample}}$$

where R = ml. ceric sulfate equivalent to 1 ml. of ferrous sulfate. (See Standardization).

or

$$\% \text{ residue} = \frac{15.7 [(\text{ml. } Ce(SO_4)_2) (N_{Ce(SO_4)_2}) - \text{ml. } Fe(SO_4) (N_{FeSO_4})]}{\text{wt. oil sample}}$$

3/8" FLARE CONNECTOR
ALTER AS SHOWN

FIN SQUARE

Rubber Gasket

1/2"

13 mm

3/8" FLARE NUT
ALTER AS SHOWN

2 mm

ENLARGE HOLE IN
NUT TO 7/16" DIA.

Rubber Gasket

FIGURE I
GLASS REACTOR

10 MM O.D. - 2MM
WALL PYREX
GAGE GLASS

73 MM

236 MM

163 MM

NO. O

1/16"

3/32" dia

1/2" dia
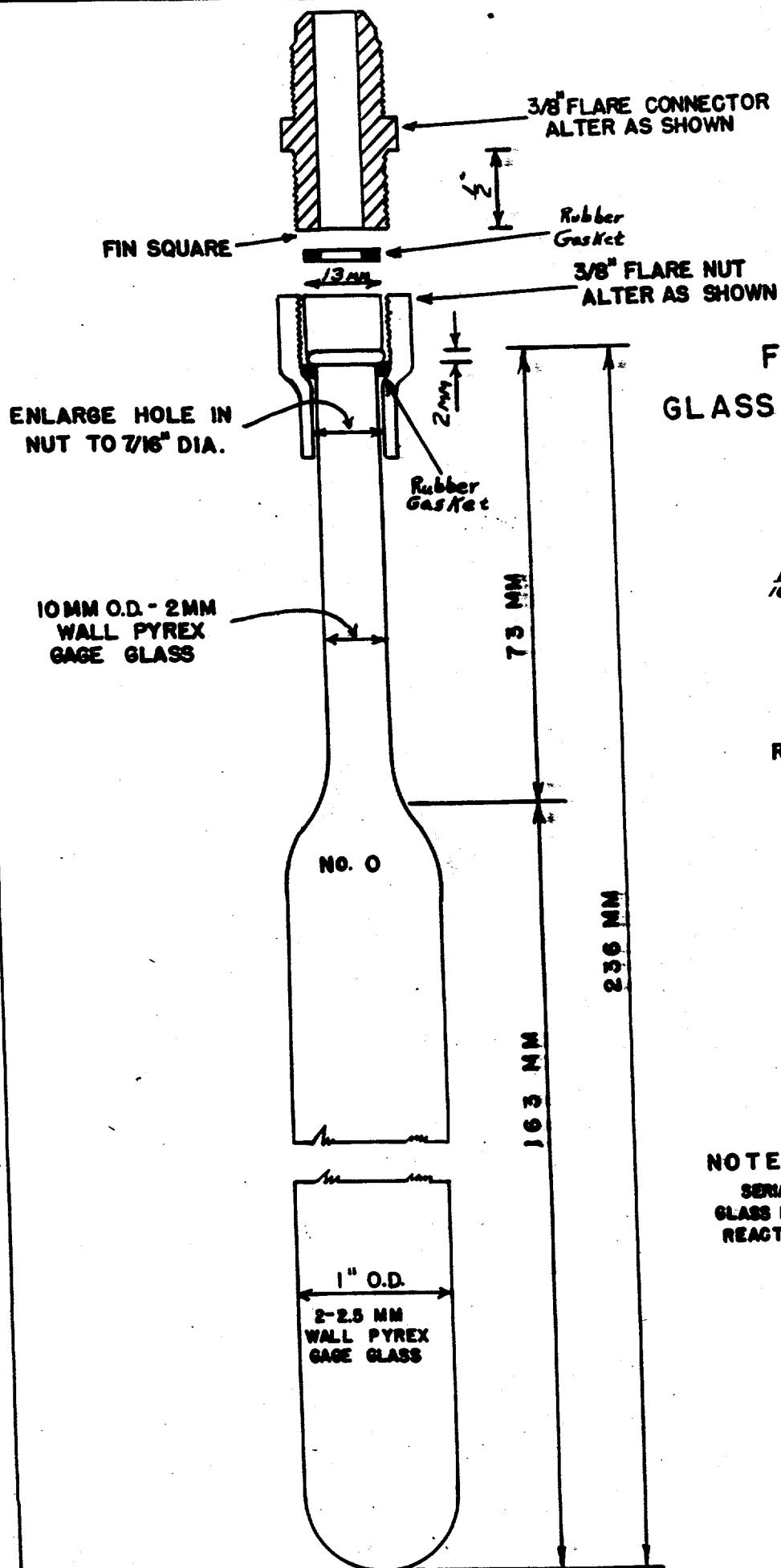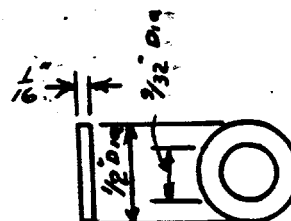
RUBBER GASKET
2 REQ'D

1" O.D.

2-2.5 MM
WALL PYREX
GAGE GLASS

NOTE -
SERIAL NOS. TO BE ETCHED ON
GLASS REACTORS. NUMBER
REACTORS CONSECUTIVELY

POTENTIOMETRIC SETUP USED IN DETERMINATION OF MFL & C-2144 INERTNESS
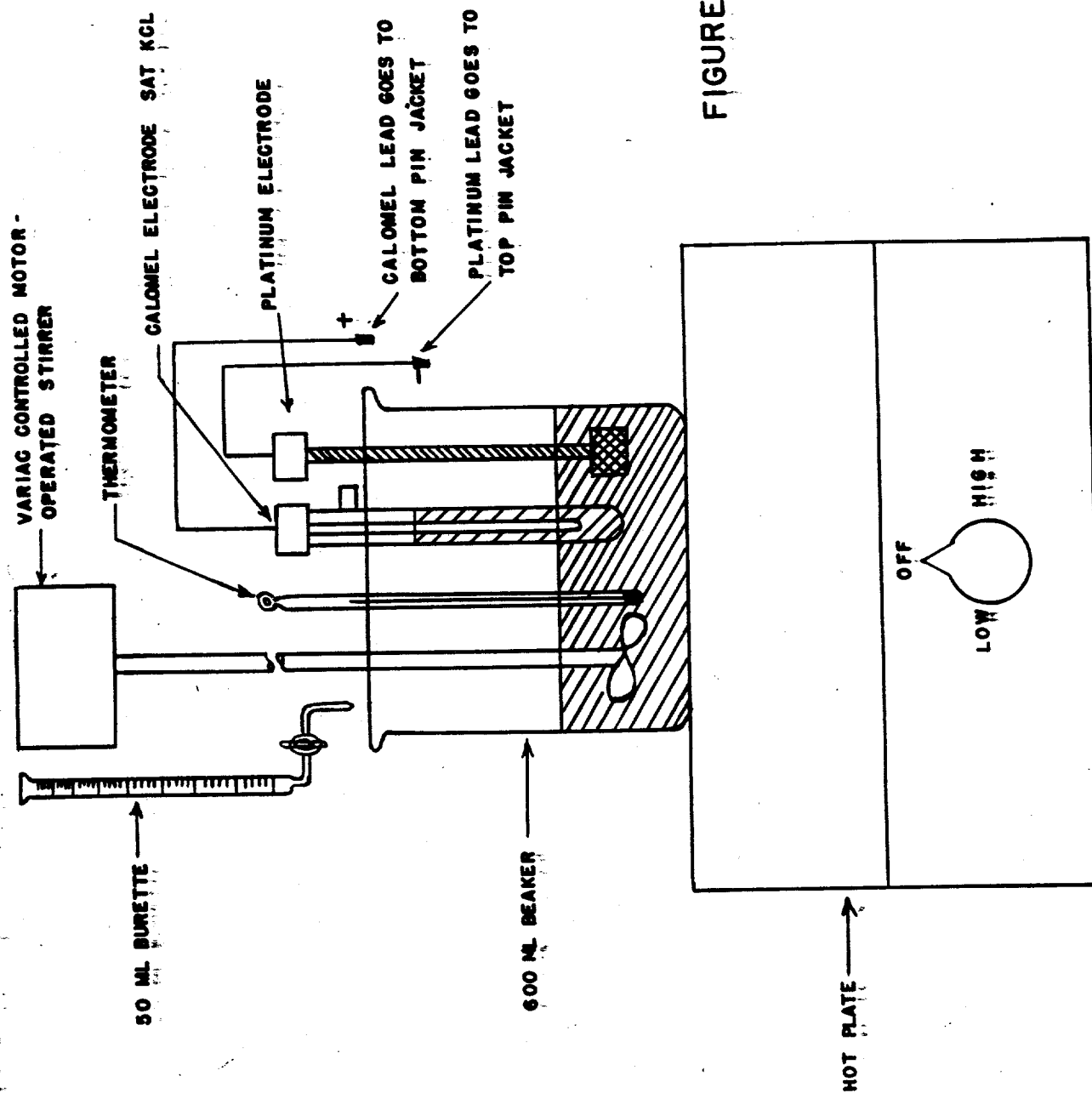
FIGURE 2

FIGURE 3

OXIDATION - REDUCTION GRAPH

OF

50 ML Ce+4 WITH APPROX. 0.01 N. Fe+2

END POINT
(45.0 ML REAGENT)

NOTE - DOTTED LINE INDICATES
EXTRAPOLATED CURVE

EMF IN MILLIVOLTS

MILLILETERS OF FERROUS AMMONIUM SULFATE

VAPOR PRESSURE ANALYSIS OF C-2144 OR MFL

A known amount of dry, oil-free nitrogen is passed through the sample at 60° C. (140° F.). Volatile material is condensed in a glass trap surrounded by dry ice and weighed. The vapor pressure is calculated from the weight of material volatilized. Three runs are made simultaneously with the present equipment.

I. Apparatus

A. Constant temperature oil bath at 60° C. $\angle 0.2^{\circ}$ C.

B. Saturators and traps as shown in Figure 1.

C. Rotameters in the range of 0-1.4 liters per minute.

D. Clean glass beads approximately 5 mm. in diameter.

E. Drying oven operating at 110° C.

F. Analytical balance.

G. Cylinder of oil and moisture-free nitrogen fitted with reducer valve.

II. Procedure

A. Assemble the apparatus as shown in Figure 2.

B. Place the sample to be run in the 60° C. bath or an oven at the same temperature one-half hour before starting the run.

C. Fill the saturator with clean, dry glass beads 5 or 6 mm. in diameter to a height of 3 inches.

D. Shake the sample to mix thoroughly and pour it into the clean saturator to just cover the beads. (Approximately 50 ml.).

E. Lubricate the saturator stopper with a small amount of the sample and insert it in the ground glass joint of the saturator.

Immerse the saturator in the medium to a depth well over the sample level, and purge for two minutes with a slow, steady flow of nitrogen.

F. Place the clean (see "Cleaning Procedures") trap that has been previously weighed on an analytical balance to 0.1 mg. (see "Weighing Traps") in position on the saturator. Lubricate the tapered ground glass joint on the trap with the sample material but not near the small end of the taper.

G. Connect the rubber tubing from the secondary trap to the rotameter. (Actually, to avoid confusion and errors, when running more than one sample at a time there is a standard arrangement of apparatus; i.e. always attach a Prest-o-lite regulator to the saturator in the same position and connect the saturator to the secondary trap which leads to the same rotameter – thus setting up three separate and distinct circuits.

H. Raise the trichlorethylene-dry ice bath around the glass trap.

I. Start the flow of nitrogen by opening the Prest-o-lite valve slowly to prevent a surge and splashing of sample. Adjust the flow until the height of the rotameter bob corresponds to 0.5 liter per minute on the calibration curve for the particular rotameter.

J. Take the following reading every half-hour:

1. Rotameter reading – these should remain constant during the run. Correct if necessary.

2. Temperature of the nitrogen leaving the rotameters.

3. The temperature of the bath.

4. The barometric pressure. (At the beginning and end of each run).

K. At the end of 4 hours close the valve on the Prest-o-lite regulator, remove the trap, and carefully wipe the lubricant from the taper joint with a clean cloth moistened with Freon 113 or acetone. Place the cap over the taper joint and a rubber policeman over the other end as quickly as possible.

L. Connect another clean, weighed trap to the saturator, and start another run into this trap from the _same_ sample.

M. Wipe the outside of the removed trap with a clean, dry towel, and place in a desiccator for one-half hour before weighing.

N. Make calculations for the two runs. If the two runs check within 2⁰ per cent of each other and are within the specifications, report the vapor pressure of the sample as an average of the two results. If the checks are poor, or if the values obtained are greater than the specifications run additional determinations.

III. Calculations

Calculate the vapor pressure according to the following equations:

$$\frac{(\text{liters of nitrogen aspirated}) (273) (P)}{(760) (273 + t)} = "a" = \text{Volume of gas aspirated at standard temperature and standard pressure.}$$

P = Barometric pressure (Average of the two readings).

t = Average temperature of aspirated nitrogen in °C.

-4-

273 = standard temperature in degrees absolute.

760 = standard pressure in mm.

$$\frac{\text{(weight of material volatilized) } (22.4) \ (760)}{(\text{"a"}) \quad (1000)} = \text{Vapor pressure of sample in mm. of Hg.}$$

Weight of material volatilized = gain in weight of trap.

22.4 = one gram molecular volume in liters.

1000 = assumed molecular weight of C-2144 or MFL.

A "reduced formula" can be used:

$$\frac{(47.4) \ (\text{weight of material volatilized) } (273 \neq t)}{(\text{liters of nitrogen aspirated) (P)}} = \text{Vapor pressure of sample.}$$

IV. Weighing Traps

Weigh traps with a similar trap as a tare and with both ends plugged. Place a ground glass joint plug on the taper end and stretch a rubber policeman over the tubing of the discharge end. Handle plugs very carefully so that their weights remain constant for both the clean weight and for the residue weight. In running three simultaneous samples, have three sets of plugs well marked and use the same plug for both weighings of the same trap.

For convenience in weighing, hang traps from the pan hangers of the balance by means of wire handles attached to the traps.

V. Cleaning Procedures

A. Traps - After using the trap, rinse it out four times with small quantities (not greater than 5 ml.) of fresh acetone. If the trap contains a very large amount of volatile material (over 50 mg.) or if sample is C-2144 it is advisable to soak

with about 10 ml. of Freon 113 for five minutes, rinse with

fresh Freon and then start the acetone rinses).

Place in the oven at 100-110° C. for 1 hour.

Remove from oven and place the trap, without the plugs

in the desiccator for at least one hour before weighing.

B. Saturators

1. Drain out as much of the oil sample as possible. (By

draining the saturator while it is still hot, most of the

sample can be recovered).

2. (a) If the oil sample was very viscous, use warm waste

Freon 113 to wash out excess oil. Then wash out the

remainder of oil with clean warm Freon 113 forcing it

back and forth through the porous filter using a rubber

sponge as a mechanical aid to this operation.

(b) If the oil sample is not very viscous, one washing

with clean Freon 113 should remove the oil.

3. Rinse thoroughly with acetone.

4. Dry saturator in the oven at 100° C. for a minimum of

1-1/2 hours.

C. Glass Beads

1. Drain the 1FL or C-2144 from beads by placing them in a

wire strainer which is placed over a beaker. The oil will

drain from the beads more rapidly if kept in an oven for

15 to 20 minutes.

2. Remove from oven, put beads in a clean beaker, add warm
   waste Freon 113 to cover the beads, stir beads well with
   stirring rod, then drain off Freon. Add clean, warm
   Freon 113 and stir. Drain.

3. Rinse well with acetone at least twice, put beads in a
   clean beaker, and place in oven to dry for a minimum of
   1-1/2 hours.

NOTES: If MFL or C-2144 sample contains any C-616 or other impurities,
wash the saturator and beads well with hot soap solution after being
washed with the hot Freon. Perform the washing with soap solution
after the washing with Freon as the Freon dissolves only the oil,
leaving the other impurities which are readily dissolved by the soap
solution).

It is permissible to use trichlorethylene as a substitute
for Freon if the sample is MFL.
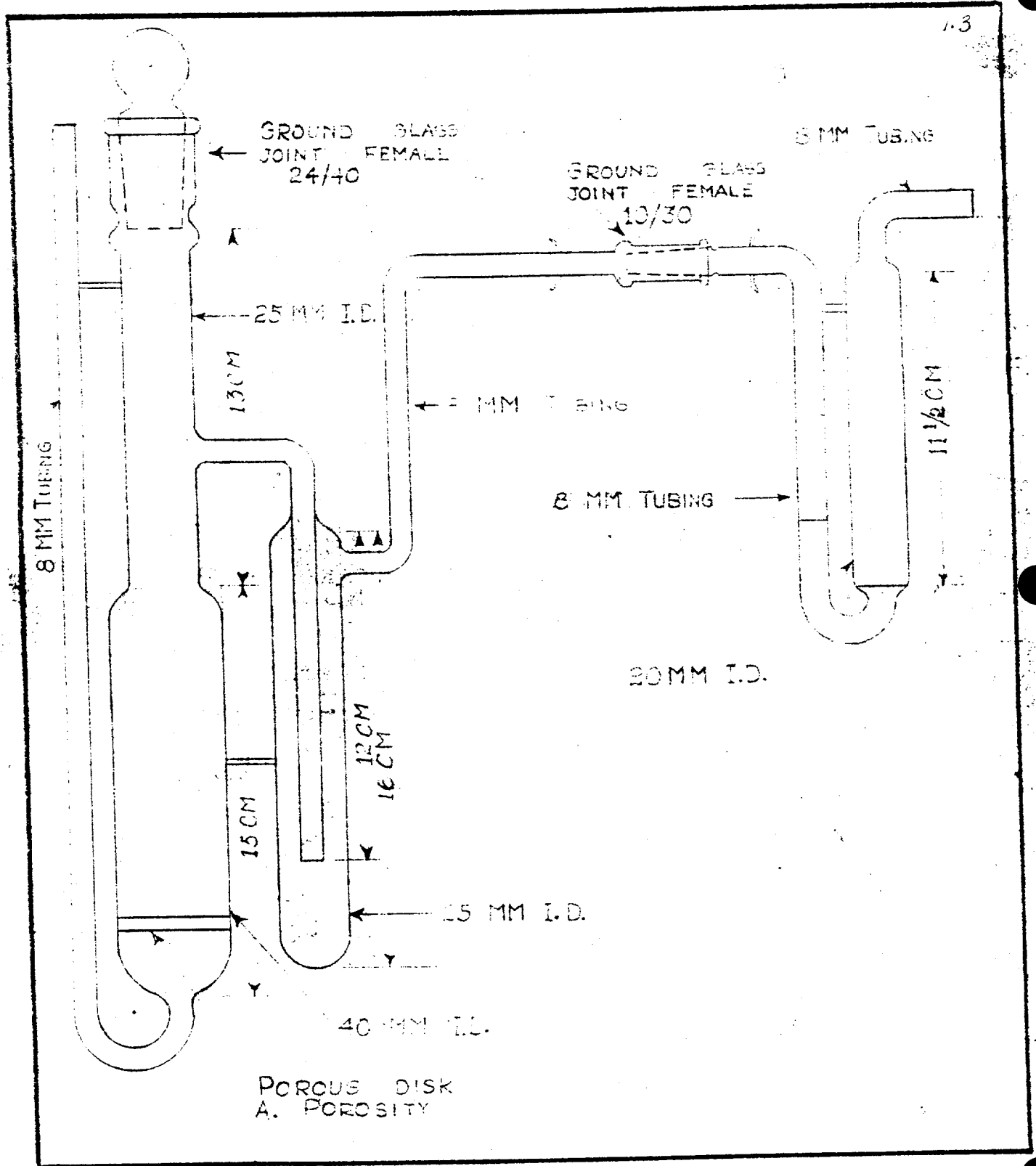
FIG. 1 SATURATOR AND TRAP FOR DETERMINING THE VAPOR PRESSURE OF MFL AND D-2144
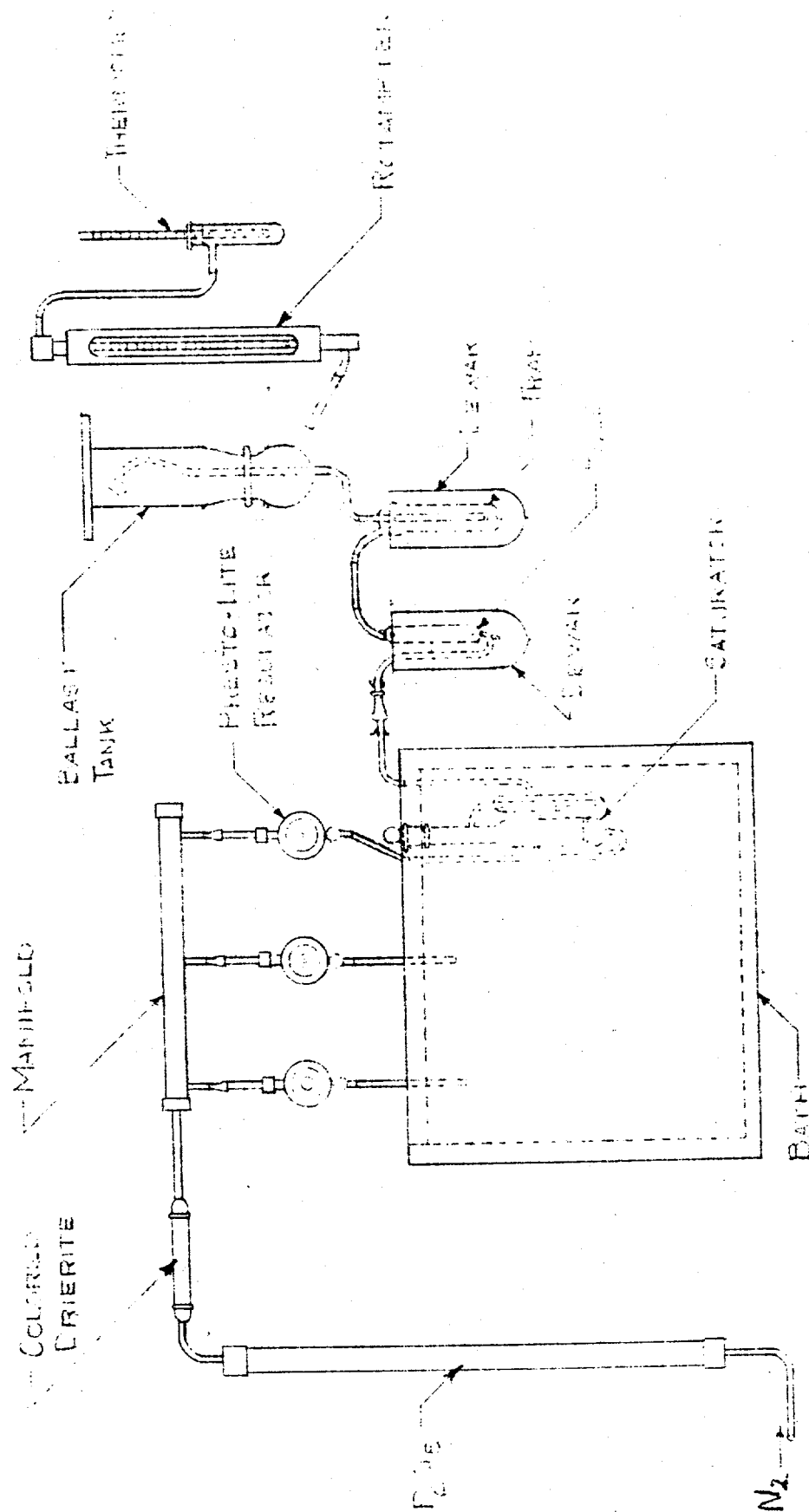
FIG. 1. DETERMINATION OF VAPOR PRESSURE OF MF1 AND 5-914 H

C-216 CONDITIONING

(See Figure 1)

I. Charging

1. Be sure equipment to be conditioned is thoroughly clean and dry.

2. Attach equipment to be conditioned to line manifold.

3. Close all valves on the apparatus.

4. Start vacuum pump.

5. Open valves on the equipment being conditioned.

6. Slowly open valves P and L and pump a 28 inch vacuum on the equipment being conditioned.

7. Close valve P.

8. Open valve on top of C-216 cylinder and then valve C, letting C-216 into the equipment being conditioned to the desired pressure.

9. Close valves on the equipment being conditioned and valve on top of C-216 cylinder.

10. Open valve N, letting G-74 into the system to a pressure of at least 30 pounds gauge.

11. Close valve N and open valve D. Then close valve D and open valve N. Repeat this alternate pressurizing and releasing ten times.

12. Close valves D and N, open valve P and pump down to 28 inches of vacuum for one minute.

13. Close valves P, L, and C. Open valve N and let G-74 into system to 5 pounds gauge pressure.

14. Remove equipment being conditioned from the manifold. It is now ready for its conditioning period, preferably 24 hrs. at 100° C.

II. Discharging

1. Place conditioned and cooled equipment on the line manifold.

2. Open valves N and L letting G-74 into the manifold to a pressure of at least 30 pounds gauge.

3. Close valve N.

4. Open valves on equipment being conditioned, then open valve D.

5. Close valve D and open valve N. Close valve N and open valve D. Repeat this alternate pressurizing and releasing ten times.

6. Close valves D and N, open valve P and pump down to 28 inches of vacuum for one minute.

7. Close valves P, L, and C. Open valve N and let G-74 into system to 5 pounds gauge pressure.

8. Remove conditioned equipment from line manifold.

NOTE: Keep hood door closed at all times that C-216 is being transferred except the times it is necessary to momentarily open or close a valve. Wear asbestos gloves during this operation.

FIGURE 1

TO TRAP & PUMP

TO HOOD DISCHARGE

SAFETY GLASS

PRESSURE GAUGE

LINE MANIFOLD

3/8 FLARE CONNECTORS

TO N₂ SUPPLY

N

P

L

C

D

BENCH 3 HOOD

C-216 CYLINDER
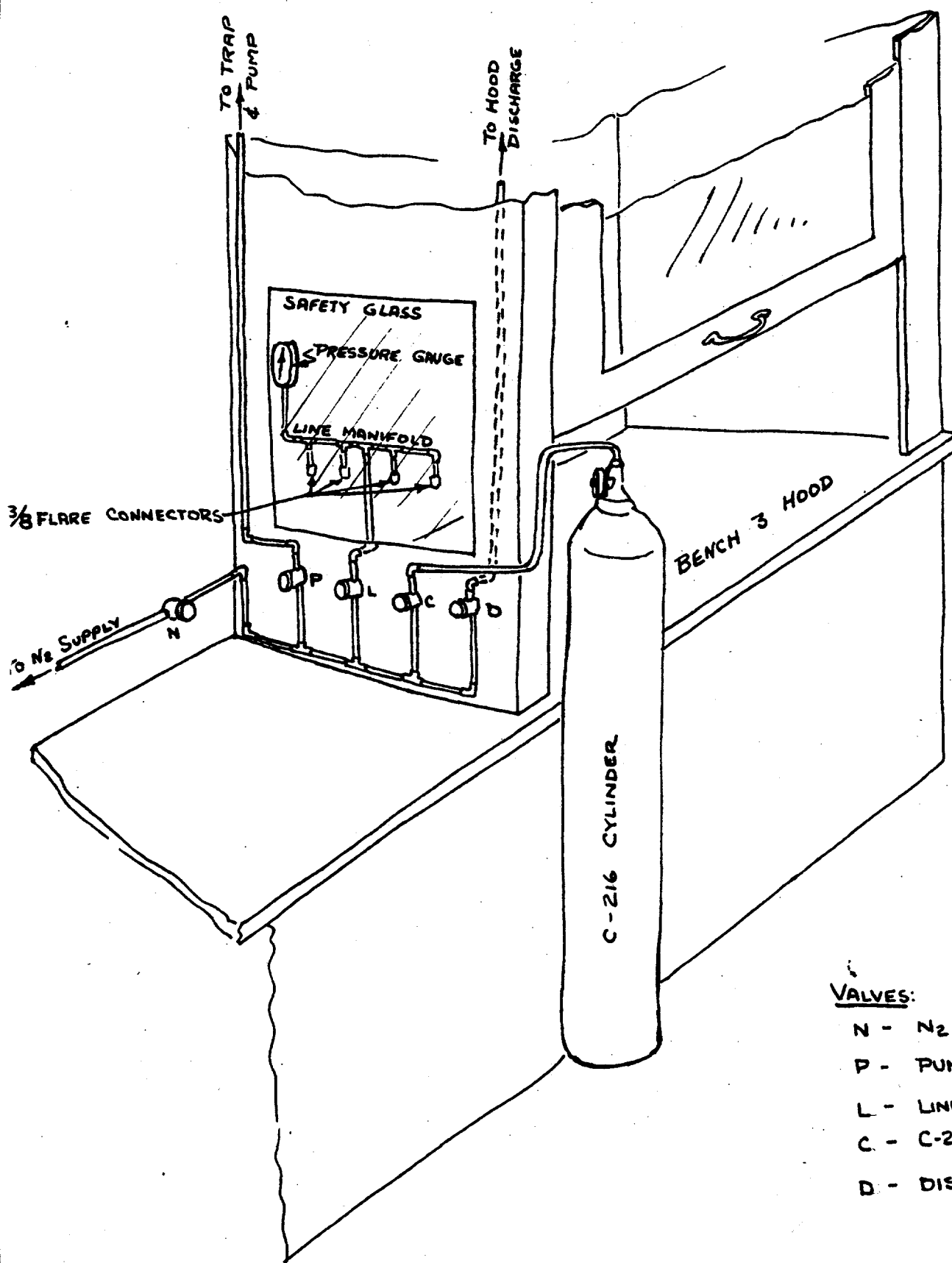
VALVES:

N - N₂

P - PUMP

L - LINE (4 ADAPTERS & PRESSURE GAUGE

C - C-216

D - DISCHARGE TO HOOD

DETECTION OF ACIDITY IN FLUOROCARBONS

(C-816, C-716, C-2144 and MFL)

I. Detection of Acidity in Distilled Water

A. Add one drop 0.1 per cent methyl orange to 10 ml. of distilled water in a clean test tube.

B. If a pink color is formed, do not use this water for detection of acidity in fluorocarbons. If no pink color is formed, proceed as in Section II.

II. Detection of Acidity in Fluorocarbon Sample

A. Add 30 ml. acid-free distilled water to a 10 ml. portion of the sample in a clean test tube.

B. Shake thoroughly and allow sample to settle.

C. Decant 10 ml. of the aqueous layer into a clean test tube.

D. Add one drop 0.1 per cent methyl orange to the aqueous portion from Step C. The formation of a pink color indicates acidity in the sample.

PROCEDURE FOR A.S.T.M. DISTILLATION

OF C-816 AND C-716

D-86-40 A.S.T.M. Part II, 1942 will be followed.

1. Recordings during the distillation will be made in
   accordance with the distillate volume rather than by
   temperature increments. Recordings, in addition to
   I.B.P. and Dry point, will be made when the distillate
   reaches the 5 ml. mark, each 10 ml. mark, and the
   95 ml. mark on the graduate.

2. The following settings have been found approximately
   correct for the Eimer & Amend Heater when distilling
   ordinary C-816.

SETTING	CHANGE POINT
95	After 4 minutes place flask on heater
60	At 90° F flask temperature
10	4 ml. level
15	9 ml. level
20	14 ml. level
30	24 ml. level
40	29 ml. level
45	39 ml. level
40	49 ml. level
35	69 ml. level
25	79 ml. level

PROCEDURE FOR CLOUD POINT TEST OF C-816 AND C-716

The standard method of test for Cloud and Pour points D-97-39, Part 3, A.S.T.M., 1942 will be used.

Normally only one bath maintained at a temperature of dry ice and tri-chlorethylene is necessary. Recording of cloud point is made at -30°F.

PROCEDURE FOR VISCOSITY TEST OF MFL, MFI, AND C-2144

Method B, D-445-39T, A.S.T.M., 1939, will be followed using a constant temperature of 210°F with the following addition:

1. Results will be reported in centipoises.

Calculation·

Viscosity $=$ Constant X Efflux time X Density

PROCEDURE FOR DETERMINING DENSITY OF FLUROCARBONS

I. Pycnometers should be of suitable design with approximately 25 ml. capacity and equipped with ground glass stoppers containing a capillary.

    A. <u>Cleaning</u> - Fluorocarbon lubricants should be rinsed from the surface of the glassware by use of freon or trichloroethylene. Dichromate cleaning solution should then be used, followed by rinsing with distilled water and acetone.

    B. <u>Drying</u> - Should be accomplished in a 100°C oven for a minimum of one and 1/2 hours, with subsequent cooling in desiccator.

    C. <u>Calibration</u> - Volume of each pycnometer at 210°F is necessary. Triple distilled mercury should be used for this operation and the weighings made as indicated below.

II. Weigh the empty pycnometer with stopper on the analytical balance.

III. Fill the pycnometer with sample to be tested, insert the stopper, excluding any air bubbles, and place it in the thermo-regulated bath for a minimum of 15 minutes to allow sample to come to temperature of bath.

IV. Wipe excess sample from top of stopper. Remove pycnometer from bath. Wipe off bath fluid, cool to room temperature and weigh.

$$\text{Density} = \frac{\underline{\text{Final wt. of pycnometer} - \text{Wt. of empty pycnometer}}}{\text{Volume of pycnometer as calibrated}}$$

MFL MIST DETERMINATION

Part B

Gravimetric Determination

This is a method for the determination of MFL mist in pump discharge after passing through a mist filter.

Part A describes the method for taking the sample into a 5 liter monel can.

Part B describes the method for the gravimetric determination of the MFL in the can.

Part C describes the determination of MFL in the can by infra-red absorption.

I. Apparatus

A. Sample cans

The samples are taken in 5 liter monel cans fitted at each end with one inch gate valves packed with D-29. (See Figure 1).

B. Platinum dishes and crucibles.

C. Oven at 60° C.

II. Reagents

A. F-113

May be used as it comes from the cylinder if 200 ml. gives a residue of 1 mg. or less on evaporation. If the blank is greater than 1 mg. the material must be distilled before use.

III. Procedure

A. Place sampling can in dry ice box on back porch for one hour.

B. Remove, open only one valve, and extract bulb with five 30-40 ml. portions of F-113.

C. Filter and wash filter with F-113

D. Place all filtrate and washing in a 200 ml. platinum dish and place in oven at 60° C.

E. When this solution has evaporated almost to dryness, transfer it (using F-113 to make the transfer) to a tared 15 or 20 ml. platinum crucible.

F. Place this crucible, containing the MFL sample in the oven at 60° C. and evaporate to dryness.

G. Weigh and subtract the tare weight to get the weight of MFL.

H. Again place crucible in oven for 30 minutes, cool in desiccator and weigh again.

I. Repeat this weighing process until the crucible has reached a constant weight.

J. After the sample has been weighed, it must be prepared for an infra-red analysis. To do this, dissolve the sample from the platinum crucible with carbon tetrachloride, and very carefully transfer it to a 10 ml. volumetric flask. Make the volume to exactly 10.0 ml. with CCl_4, stopper, tag with proper number, and put in safe place. The day shift will turn samples over to the infra red group.

IV. Calculations

A. The temperature of these samples will be given in degrees Fahrenheit. Convert to degrees Centigrade as follows:

$$°C. = 5/9 \ (°F.-32)$$

B. Then when P = barometric pressure

$$mg. \ MFL/cu. \ ft. \ (STP) = \frac{(mg. \ MFL \ in \ sample) \ (78,840) \ (T° \ C+273)}{(Vol. \ bulb \ in \ 1l.) \ (P)}$$

These results will be reported as mg. MFL/cu. ft. (STP).

C. Derivation of above formula:

$$\text{mg. LFL/cu.ft. (STP)} = \frac{\dfrac{\text{Mg. LFL in sample}}{(\text{Vol. bulb in ml.}) (P) (273)}}{(760) (t^{\circ}C. + 273) (1000) (28.32)}$$

and clearing the formula given above is obtained.
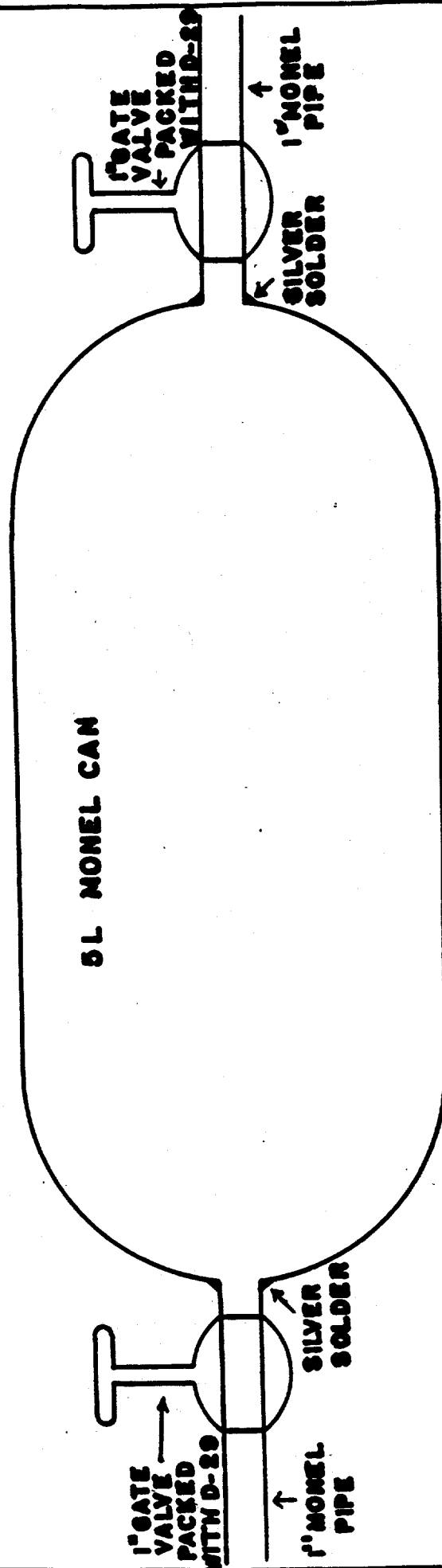
5L MONEL CAN

1"GATE VALVE PACKED WITH D-20

1" MONEL PIPE

SILVER SOLDER

1"GATE VALVE PACKED WITH D-20

1" MONEL PIPE

SILVER SOLDER

FIGURE 1

SAMPLE CAN FOR MFL MIST ANALYSIS

DETERMINATION OF MFL MIST

PART C

Infra Red

Two standard samples must be prepared. The first is a sample of pure, dry carbon tetrachloride. The second is another sample of the same carbon tetrachloride to which approximately 20 milligrams per milliliter of MFL have been added. This concentration should be known to at least three significant figures.

NOTE: The carbon tetrachloride used in the preparation of unknown samples must be from the same source as that used in the standard samples.

A salt cell of 0.18 mm. thickness is used, although the thickness is by no means critical.

I. Adjustment of Apparatus

1. Prepare the equipment for use with the optical amplifier, as directed in "Operation of Infra-Red Spectrometer".

2. Set the spectrometer at 13.00 on the wavelength dial, and the slit width at 0.200 millimeters.

3. Set the amplification of the galvanometer system to give a deflection of about 300 millimeters, with the cell out of the light path.

II. Operation

1. Fill the salt cell with some of the solution containing 20 mg. per ml. MFL

2. Adjust the wavelength dial to the point giving minimum galvanometer deflection in the vicinity of 13.00.

3. Record this setting of the wavelength dial, and keep it constant during the series of samples.

NOTE: "Deflection" is defined as the difference between the galvanometer readings with the shutter open and closed, respectively.

4. Take galvanometer readings for this known sample as follows:

    (a) Cell in position, shutter open.

    (b) Cell in position, shutter closed.

    (c) Cell out, shutter open.

    (d) Cell out, shutter closed.

5. Repeat these at least twice, until a sufficient number have been taken to give the desired accuracy.

6. Remove the solution from the absorption cell by means of an aspirator, taking care to prevent water from coming in contact with the salt cell.

7. Flush the cell out with two portions of pure carbon tetrachloride to remove any residual MFL.

    (a) Unless the samples are known to be of low concentration (5 mg./ml.) the cell should be flushed with pure carbon tetrachloride after every sample.

    (b) Special care must be taken when a strong (10 mg./ml.) solution is to be followed by a weaker solution or pure solvent.

8. Fill the cell with pure carbon tetrachloride, and take galvanometer readings as before.

9. Place the unknown samples successively in the absorption cell, and take readings.

10. After every second or third unknown, the standard carbon tetrachloride is rerun. There should be less than 1 per cent difference

between successive runs. If greater differences are encountered, run the standard more often, taking special care to avoid contamination.

11. The entire series of unknowns should be run through twice, not necessarily on the same day. If a difference of more than 0.2 mg./ml. exists between the two measured values for any unknown, it should be rerun until satisfactory agreement is obtained.

III. Calculations

A. Concentrations of MFL less than 35 mg./ml.

1. For each pair of galvanometer readings subtract the reading with the shutter closed from that with the shutter open. This gives the "galvanometer deflection".

2. Divide deflection with the cell in position by the deflection with the cell removed to get the transmission.

3. Average the transmissions for the several observations of the standard samples of CCl_4 and use this average in all subsequent calculations.

4. Divide the transmission for each sample, including that containing a known quantity of MFL, by the averaged transmission for pure carbon tetrachloride. This gives the transmission of the dissolved MFL, the absorption due to carbon tetrachloride and the cell walls having been corrected for.

5. Find the logarithms of these corrected transmissions from the table.

6. Divide the logarithm of the solution of known MFL concentration by that known concentration, in milligrams per milliliter.

7. Record this factor, denoted by "F", to three significant figures.

    (a) With the apparatus and method described, "F" is usually approximately 0.024.

8. Divide the logarithm for each sample by "F".

9. The resulting number is the concentration of MFL in milligrams per milliliter in the sample.

10. Multiply by the volume of the total sample, in milliliters, giving the total milligrams of MFL in the sample. Samples submitted are usually 10 milliliters.

11. Average the amount of MFL in each sample series of runs.

12. Report the calculated values and the average.

13. If the concentrations differ by more than 0.2 mg./ml. run the sample again, and average all the values, unless it is obvious that one of the values is in error.

B. Concentrations of MFL greater than 35 mg./ml.

The above method of calculation has been found experimentally to be valid only up to concentrations of about 35 mg./ml. of MFL. Above this concentration the transmission of the sample is so low that scattered radiation of shorter wavelengths reaching the thermocouple causes a continually increasing error. For these higher concentrations the following techniques are used:

1. 35-70 milligrams per milliliter.

    (a) Calculate as above through Step 3, the calculation of averaged transmission fractions.

    (b) Subtract the factor 0.015 from each transmission fraction, including those for the known samples.

(c) Calculate the remaining Steps (4-13), as above, using these compensated transmission values.

(d) NOTE: This method is quite valid for concentrations below 35 mg./ml., and no error is caused by its use for dilute samples.

2. Over 70 milligrams per milliliter.

(a) Estimate, by the method used for samples containing 35-70 mg./ml., the approximate MFL content of the unknown sample.

(b) Divide the resulting MFL content (in mg./ml.) by 20, giving the number of milliliters of pure carbon tetrachloride to which one milliliter of sample would have to be added to bring the sample well within the experimental range of concentrations.

(c) Add 1 milliliter of the unknown sample by means of a pipette to the above calculated number of milliliters of carbon tetrachloride, of the same lot as that used in preparing the original sample.

(d) Rerun the sample by the usual method.

(e) Calculate the concentration of the diluted sample by the method used for samples containing 35-70 mg./ml.

(f) If the concentration is still above 70 mg./ml. repeat the dilution process.

(g) If the concentration calculated is below 70 mg./ml., multiply by the dilution factor (the number of milliliters of solution resulting from the dilution of the one milliliter of sample with pure carbon tetrachlorde), and report the resulting true concentration.

(h) If it is necessary to repeat the dilution process, multiply the concentration measured by the product of the successive dilution factors.

IV. Sample Calculations

1. Below 35 milligrams per milliliter.

For sample "Std. CCl$_4$"

Average transmission for first run: $\dfrac{.620 \,/\, .622 \,/\, .620 \,/\, .622}{4} = .621$

Average transmission for two runs: $\dfrac{.621 \,/\, .613}{2} = .617$

For sample "Std. CCl$_4$ $\neq$ 22.62 mg./ml. MFL

Average transmission: .161

Transmission corrected for pure CCl$_4$: $\dfrac{.161}{.617} = .261$

Log transmission: -0.58336

$F = $ logarithm for 1 mg./ml. $= \dfrac{-0.58336}{22.62} = .0258$

For sample No. 241

Average transmission: .561

Corrected transmission: .909

Logarithm of transmission: -.04144

Concentration: $\dfrac{-.04144}{-.0258} = 1.61$ mg./ml. MFL

Sample	Average Transmission	T/T Pure	Log. (corr. T)	Mg./ml. MFL
CCl$_4$ $\neq$ 22.62 mg./ml. MFL	0.161	0.261	-0.58336	
Std. CCl$_4$	0.621			
No. 241	0.561	0.909	-0.04144	1.61
No. 243	0.606	0.982	-0.00789	0.31
Std. CCl$_4$	0.613			

Slit: 0.200
Dial: 13.00
F: -0.0258
TCCl$_4$: .617

Original data on pages 14-15, Book BL-245

2. 35-70 milligrams per milliliter

Sample	Average Transmission	A.T. -0.015	Corrected Transmission	Log Trans.	Mg./ml. MFL
Std. CCl₄ / 22.62 mg./ml. MFL	.161	.146	.242	-.6162	
Std. CCl₄	.619	.604			
Unknown	.0320	.0170	.0282	-1.5498	56.7

$$F = -.0273$$

3. Over 70 milligrams per milliliter

Sample	Average Transmission	A.T. -0.015	Corrected Transmission	Log Trans.	Mg./ml. MFL
Std. CCl₄ 22.62 mg./ml. MFL	.166	.151	.247	-.6073	
Std. CCl₄	.627	.612			
Unknown	.0212	.0062	.0038	-2.4202	90

$$F = -.0269$$

Dilution: $\frac{90}{20} = 4.5$.

Dilute 1 ml. sample in 4 ml. of CCl₄, giving a dilution factor of 5.

Rerun

Sample	Average Transmission	A.T. -0.015	Corrected Transmission	Log Trans.	Mg./ml. MFL
Std. CCl₄ / 22.62 mg./ml. MFL	.166	.151	.247	-.6073	
Std. CCl₄	.627	.612			
Unknown, diluted	.203	.188	.307	-.5129	19.1

$$F = -.0269$$

19.1 x 5 = 95.5 mg./ml. MFL in original sample.

<u>C-714 IN C-816</u>

<u>Infra Red Spectrometer</u>

I. Apparatus

Determinations of percentage of C-714 in C-816 are made with the infra red spectrometer, using the galvanometer system.

The cell used is of NaCl, and has a thickness of 0.01 to 0.02 milli-meters between faces when held in its clamp. It should have a transmission of 20-45 per cent when filled with pure C-816 at the 860 cm.$^{-1}$ point.

II. Procedure

1. Set the spectrometer slit at 0.500 millimeters and the wave-length dial at 8.60.

2. Set the amplification to give a galvanometer deflection of about 200 millimeters on the scale. "Deflection" is the difference between galvanometer readings with the shutter open and closed, respectively.

3. Fill the absorption cell with standard C-816 (Lot 120).

4. Place absorption cell in position in the spectrometer.

5. Adjust the wavelength dial until a point of minimum deflection is found, usually within 5 small scale divisions of 8.60. This is the 860 cm.$^{-1}$ point.

6. Record the dial reading and keep the setting constant while running the series of samples.

7. Take galvanometer readings as follows:
    a. Cell in position, shutter open
    b. Cell in position, shutter closed
    c. Cell removed, shutter open
    d. Cell removed, shutter closed

8. Repeat this once, or until a sufficient number of readings have been taken for the desired precision. The two readings should be within 1 per cent of each other.

9. Remove the sample completely from the cell by means of an aspirator or vacuum pump, taking care that no water touches the salt cell. Since the substances in the samples are all volatile there will be no film of residue left.

10. Place a sample of standard C-816, to which a known quantity of C-714 ($\emptyset$-toluene) has been added, in the cell; and take transmission readings, as for the standard.

11. Place a sample of each of the unknown lots of C-816 in the cell, and take transmission readings as before.

12. When observations have been made for all the unknowns, run the standard sample and the sample with the known percentage of C-714 again.

13. Set the spectrometer slit at 0.400 millimeters, and the wavelength dial at 10.55.

14. Reset the amplification dial to give about 200 millimeters galvanometer deflection.

15. Put a sample of 20 per cent C-714 in C-716 in the absorption cell, and set the dial to a point of minimum deflection in that region.

16. Record the actual reading of the wavelength dial at this point and keep it constant during the subsequent samples. This is the 975 cm.$^{-1}$ point.

17. Empty the absorption cell and flush it out with pure C-816.

18. Run the same series of known and unknown samples as at the 860 cm.$^{-1}$ point; starting with pure standard C-816 and C-816 with known C-714 content, and proceeding through the unknowns, and repeating the standards at the end.

18. Make two series of runs at each of the two settings, determining the position of each setting and other adjustments anew for each, making two independent series of results.

III. Calculation

1. Divide the galvanometer deflection with the cell in the light path by the deflection with the cell out, for each set of four readings. This gives an uncorrected transmission measurement.

2. Average the transmissions for the different successive readings of each individual sample, excluding wild values.

3. Average together the initial and final averages for each of the two known samples.

4. Multiply these average transmissions by a factor, approximately 1.1, which corrects for absorption and reflection by the cell faces. This factor is equal to the reciprocal of the transmission of the cell at 975 cm.$^{-1}$ when filled with carbon tetrachloride or carbon disulfide, and changes only slowly under ordinary circumstances.

5. Obtain the logarithm of each corrected transmission fraction from the table.

6. For the calculations, pair the values, matching each series of values for 975 cm.$^{-1}$ with a series for 860 cm.$^{-1}$.

7. Divide the logarithm of the transmission for the standard pure C-816 at 975 cm.$^{-1}$ by the logarithm for the same substance in the corresponding series of 860 cm.$^{-1}$ readings. This quantity is designated as "B".

8. Multiply the logarithm for each sample in the series of 860 cm.$^{-1}$ runs under consideration by "B".

9. Subtract these products from the corresponding logarithms at 975 cm.$^{-1}$. The resulting differences are proportional to the percentage of C-714 in the samples.

10. Divide the difference, in the case of the sample of known C-714 content, by that known percentage; to obtain a quantity "C", representing the difference in the logarithms which would result from 1 per cent of C-714 in the C-816.

11. Divide the difference for each sample by "C", giving the per cent of C-714 in the sample.

12. Follow the same procedure with the other series of observations.

13. Average the resulting per cents with the others.

14. Report these per cents and averages.

15. If there is more than 1 per cent difference between the calculated per cents for any sample, rerun that sample.

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SAMPLE CALCULATIONS

C-714 in C-816

For Standard Sample No. 120 at 860 cm.$^{-1}$

$$60 - 9 = 51 \quad \text{deflection with cell in}$$
$$206 - 15 = 191 \quad \text{deflection with cell out}$$

$$51 \div 191 = .267 \quad \text{transmission}$$

$$\frac{.267 + .266 + .268 + .270}{4} = .268 \quad \text{average transmission for first sampling}$$

$$\frac{.268 + .263}{2} = .266 \quad \text{average transmission for sample}$$

$$.266 \times 1.151 = .306 \quad \text{corrected transmission}$$

$$.5143 \quad \text{logarithm of transmission (from table)}$$

For No. 120 at 975 cm.$^{-1}$

$$120 - 14 = 106 \quad \text{deflection with cell in}$$
$$215 - 14 = 201 \quad \text{deflection with cell out}$$
$$106 \div 201 = .527 \quad \text{transmission}$$

$$\frac{.528 + .516}{2} = .522 \quad \text{average transmission}$$

$$.522 \times 1.151 = .601 \quad \text{corrected transmission}$$

$$.2211 \quad \text{log transmission (from table)}$$

$$\frac{\log \text{ at } 975}{\log \text{ at } 860} = \frac{.2211}{.5143} = .4299 = \text{factor "B"}$$

For No. 120 + 4.69 Per Cent C-714

$$\log \text{ at } 975 - B (\log \text{ at } 860) = .3316 - .4299 (.4989) = .3316 - .2145 = .1171$$

$$\frac{.1171}{\% \text{ C-714}} = \frac{.1171}{4.69} = 0.02497 = \text{"C" (logarithm for sample containing 1.0\% C-714)}$$

For unknown sample No. 240, first series

$$\log \text{ at } 975 - B(\log \text{ at } 860) = .1012$$

$$\frac{.1012}{C} = \frac{.1012}{.02497} = 4.05\% \text{ C-714}$$

For No. 240, second series

4.09% C-714

Averaging results of two series

$$\frac{4.09 + 4.05}{2} = 4.07\% \text{ C-714}$$

Reported Results

Run 1   4.0% C-714

Run 2   4.1

Av.   4.1% C-714

Original data in Book BL-198, pages 30 to 37.

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TENTATIVE PROCEDURE

C-716 DISTILLATION & RESIDUE BY EVAPORATION

Apparatus:

A description of apparatus may be found in Scott's Standard Methods of Chemical Analysis, Fifth Edition, Volume II, pp. 1705-1713.

Procedure:

Distillation:

The condenser bath shall be filled with ice, and enough water added to cover the condenser tube. The temperature shall be maintained between 32°F and 40°F.

100 ml. of C-716 shall be measured in a 100 ml. graduated cylinder and transferred directly to the distillation flask. None of the liquid shall be permitted to flow into the vapor tube.

The thermometer, provided with a cork, shall be fitted tightly into the flask so that it will be in the middle of the neck and so that the lower end of the capillary tube is on a level with the inside of the bottom of the vapor outlet tube at its junction with the neck of the flask. The thermometer shall be approximately at room temperature when placed in the flask.

The flask shall be placed on the opening in the asbestos mat with the vapor outlet tube inserted in the condenser tube. A tight connection may be made by means of a cork through which the vapor tube passes. The position of the flask shall be so adjusted that the vapor tube extends into the condenser tube not less than 1 inch nor more than 2 inches.

The graduate used in measuring shall be placed without drying at the outlet of the condenser tube and shall extend into the graduate at least .

1 inch but not below the 100 ml. mark. The top of the graduate shall be covered closely during the distillation with a piece of blotting paper, cut so as to fit the condenser tube tightly.

Heat shall be applied at a uniform rate, so regulated that the 1st drop of condensate falls from the condenser in not less than 5 nor more than 10 minutes. When the 1st drop falls from the end of the condenser the reading of the thermometer shall be recorded. The receiving cylinder shall then be moved so that the end of the condenser tube shall touch the side of the cylinder. The heat shall then be so regulated that the distillation will proceed at a uniform rate of not less than 4 nor more than 5 ml. per minute. The reading of the thermometer is recorded when the 1st drop distills over. Then the reading of the thermometer is recorded when 5 ml. have distilled over and also recorded when the distillate reaches each 10 ml. mark on the graduate.

No adjustment of the heat shall be made after the liquid residue in the flask is approximately 5 ml. unless the time required to bring over the last 5 ml. of distillate and to reach the end-point exceeds 5 minutes. The end-point is the temperature reached when the flask becomes dry.

Data Reported:

The temperature is recorded with the total number of ml. distilled over.

The cooled residue shall be poured from the flask into a small cylinder graduated in 0.1 ml. and the volume recorded as residue.

The difference between 100 ml. and the sum of the recovery and the residue shall be calculated and recorded as distillation loss.

The time is also recorded each time the temperature reading is recorded.

Requirements for Duplicates:

If duplicates are run, the results obtained for the 1st drop and end-point, respectively, shall not differ from each other by more than 6°F. Duplicate readings of the volume of distillate collected when each of the prescribed temperature points is reached shall not differ from each other by more than 2 ml.

The actual barometric pressure shall be recorded, but no correction made except in case of dispute.

Residue by Evaporation:

Place 50 ml. of C-716 in a tared evaporating dish which has been dried 1/2 hour in the oven, placed in desiccator to cool and then weighed. Evaporate sample to dryness on steam bath and place in oven 1/2 hour. Cool in desiccator and weigh. All weighings should be made to the nearest 0.0001 gm.

Calculations:

Residue = difference in weight

$$\% \text{ Residue} = \frac{\text{wt. of sample}}{(\text{vol. of sample})(\text{sp. g. of C-716})} \times 100$$

The residue is tested with ultra-violet light to see if there is any oil present.

CONSTRUCTION OF THERMOPILES

The following technique for constructing ten junction copper-constantan thermopiles has been successfully used by the Sampling Department.

I. Equipment and Tools Needed

Wire: Copper wire (special high purity thermopile – grade No. 36) – approximately 115 feet.

Constantan No. 30 – approximately 80 ft.

Glass: 1 piece pyrex tubing OD 6 mm., ID 4 mm., – 1 ft.

1 piece pyrex tubing OD 8 mm., ID 6 mm., – 1 ft.

21 very small capillaries for covering the individual junctions

Friction tape

Jack knife

Small scissors

Glyptal

Soft solder – plain

Soft solder-rosin flux

Soldering iron

Thermopile jig – See Figure I

Spool of thread

II. Procedure

A. Construct the jig as shown in Figure I and mount it securely on a table, or preferably between two tables.

B. Place the copper and constantan wires on the jig as shown in Figure 2.

C. Pair the wires, copper-constantan, as illustrated in Figure 2. Tape each pair of wires together near the ends with small pieces of friction tape.

When this pairing has been done, check the complete system to be sure that the pairing is correct. If it is not, an incompleted circuit will result, and time and effort will have been wasted.

D. Cut the wires at the nails on one end as shown in Figure 3. Place the ends evenly, tape them together and tape securely to one of the nails. Pull the wires fairly taut, cut and tape the opposite ends in a similar manner. The object is to have all of the wires together as a cable, without kinks, twists, and other distortions which might later cause a break.

E. Wrap the cable with thread, as shown in Figure 4, beginning and ending approximately 6 inches from the ends. The copper leads should extend from the center of the thermopile as shown in Figure 4.

F. Remove the thermopile from the jig and make the metal junctions, observing the following points:

1. Strip the insulation back the same distance on each wire (about 3/4 inch).

2. In stripping the insulation from the wires, do not permit the cut ends to fray.

3. Remove both the cloth insulation and the varnish from the wire.

4. The copper wire is far more delicate than the constantan, so handle accordingly.

5. Make the junction as shown in Figure 5.

6. To solder the junction, dip the twisted end into the flux, then quickly pull it through a small drop of solder on the iron. This results in a _thin_ coat of solder. Drops or thick coats will make the junction too large.

G. Cut all junctions off to exactly the same length. The uninsulated
portions should not exceed 1/4 inch in length. If all of the junctions
are not the same length the temperature reading cannot be considered as
the temperature at one particular point. The junctions, if uneven or
if the insulation becomes frayed, must all be cut off, and the process
repeated.

H. Finish wrapping the cable to within one inch of the ends.

I. Draw out small glass capillaries, approximately 3/8 inches
long, from 10 mm. pyrex tubing, seal one end and fit snugly over each
junction. Use caution to prevent the cutting of the fine wires and to
see that the junctions extend to the ends of the capillaries. (Figure 6).

J. Test to see if the whole unit of ten junctions will fit into the
6 mm. tube (ID 4 mm.). Test to see if the eleven junction end, which has
the copper-copper junction, will fit into the 8 mm. tube. If the units
fit satisfactorily, paint the glass covered junctions lightly with
glyptal, and tie them together. When dried together, they will become
a more substantial unit.

K. Paint 14 inches of each end of the cable with glyptal and
dry as straight as possible. When dry, place in a drying oven at
100° C. and anneal for at least eight hours. Then remove the thermopile
from the oven and cool.

L. Test the thermopile for a complete circuit with an ohmmeter.
The resistance of the complete unit should be approximately 250 ohms.

M. The thermopile is now ready for installation and calibration.

FIGURE 1
THERMOPILE JIG

Nails for winding
and holding wires.

Nails for winding
and holding wires.

8½"

Made from scrap 2"x 4"
stock.
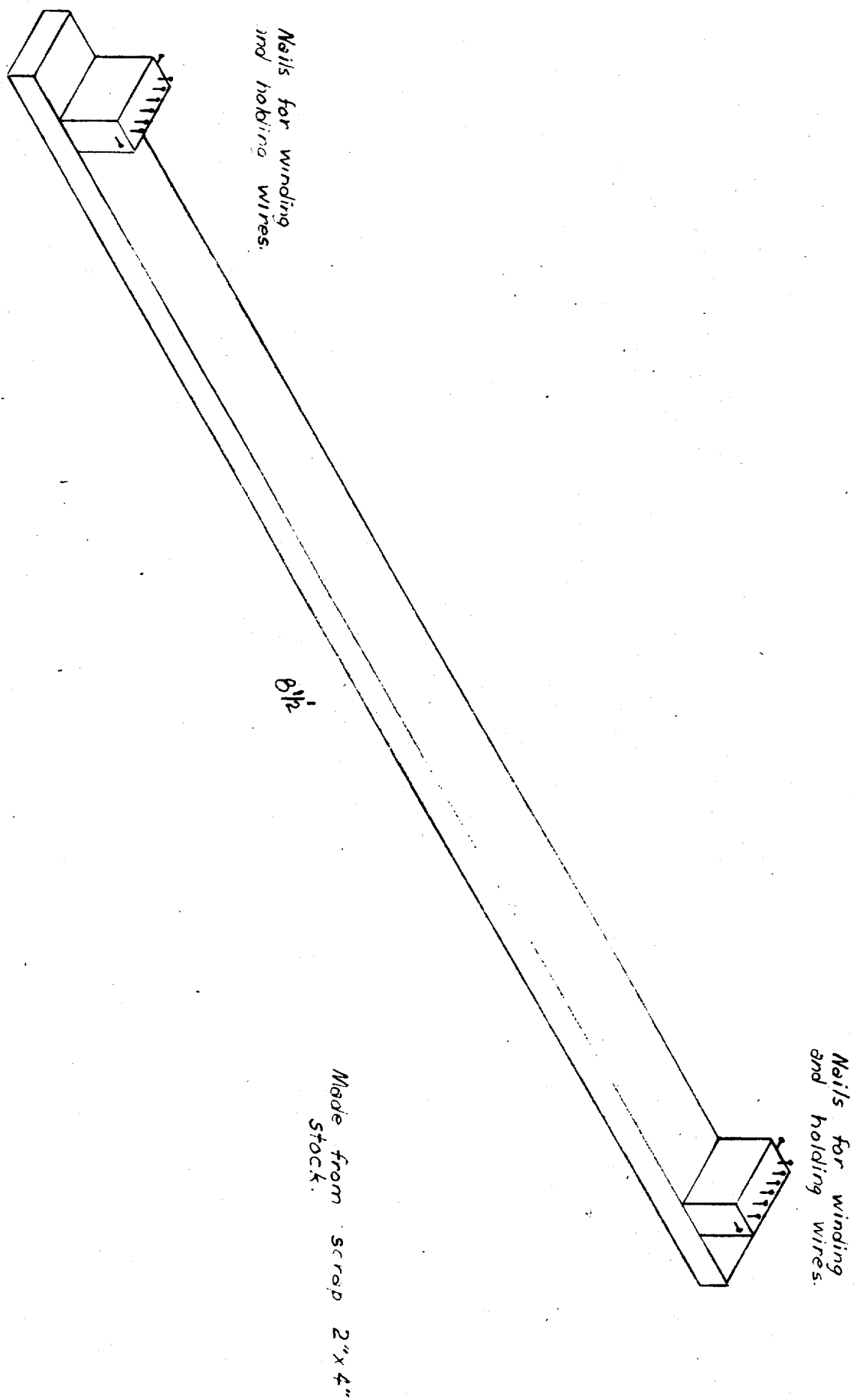
FIGURE 2

METHOD OF STRINGING AND PAIRING WIRES
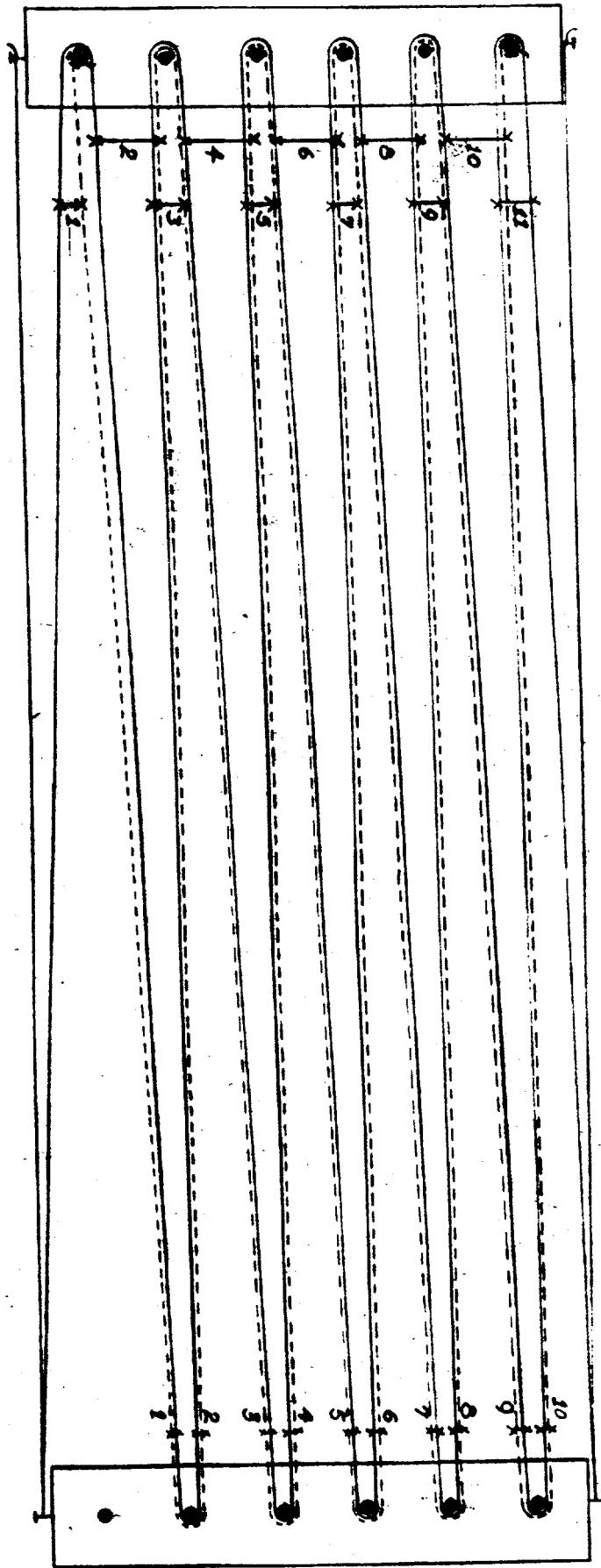
KEY:

————	NO. 36 Copper
– – – –	NO. 30 Constantan
——x——	Junction
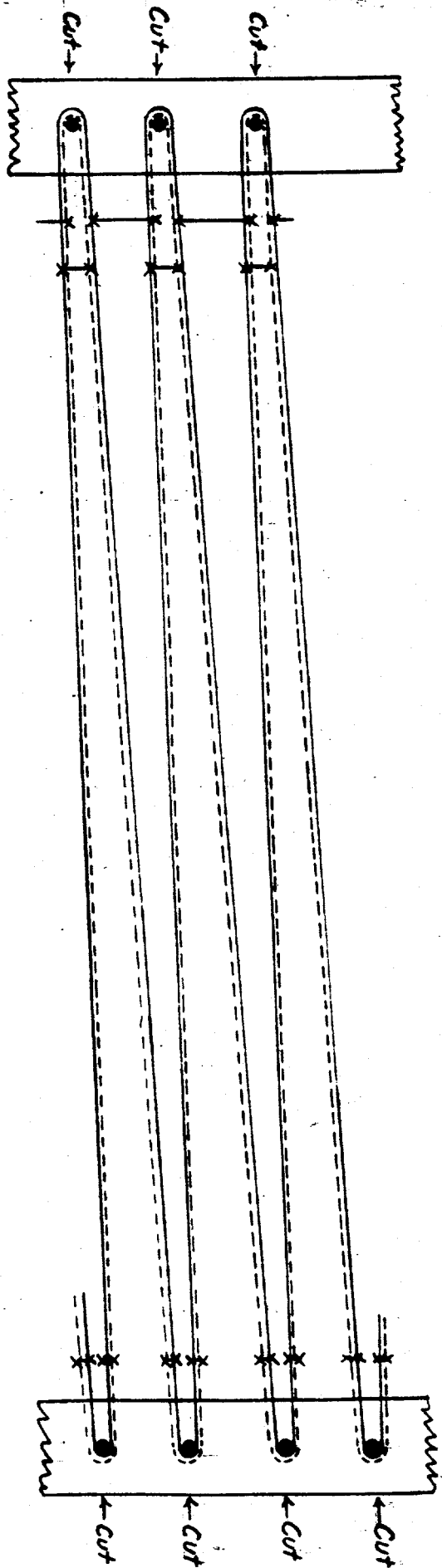
FIGURE 3

— FIGURE 4 —

METHOD OF THREAD-WRAPPING THE CABLE

FIRST WRAPPING

COPPER LEADS

SECOND WRAPPING

CABLE OF BUNCHED WIRES
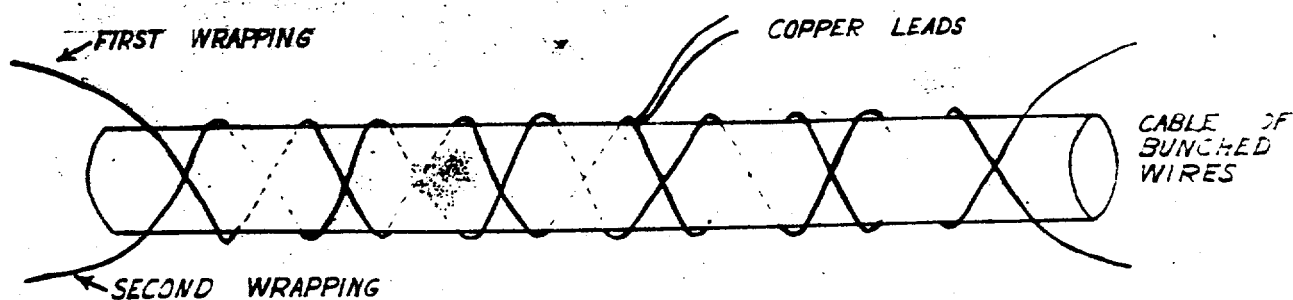
— FIGURE 5 —

METHOD OF MAKING JUNCTION

WIRES TWISTED TIGHTLY TOGETHER, STARTING AS CLOSE TO THE INSULATION AS POSSIBLE

— FIGURE 6 —

METHOD OF CAPPING JUNCTION

GLASS CAPILLARY

CALIBRATION OF THERMOPILES

I. Introduction

Before a thermopile can be used for thermal measurement, its e.m.f.-temperature relationship must be determined for the required range. This procedure is intended to give in detail the method employed for calibrating the thermopiles used in the determination of the freezing point of C-616 samples.

These thermopiles are calibrated against a reference thermopile, referred to as a secondary standard, which is not used for any operation other than calibration. The e.m.f.-temperature relationship for the secondary standard was obtained by comparison with a primary standard, a platinum resistance thermometer calibrated by the National Bureau of Standards.

II. Calibration of the Secondary Standard Against the Platinum Resistance Thermometer

1. The platinum resistance thermometer and the hot junction of the secondary standard are immersed in the same bath, and measurements of the resistance of the platinum resistance thermometer, and the e.m.f. of the thermopile made simultaneously.

2. The temperature equivalent to the e.m.f. of the thermopile is determined by calculating the bath temperature from the observed resistance of the platinum resistance thermometer.

III. Apparatus

A schematic diagram of the apparatus for calibrating the secondary standard thermopile is shown in Figure 1 and listed as follows:

Item A is a Leeds and Northrup K-2 potentiometer for measurement of the e.m.f. of the secondary standard.

Item B is a Leeds and Northrup (G-2) Mueller bridge for measurement of the resistance of the platinum resistance thermometer.

Items C show the Leeds and Northrup HS galvanometers. They are mounted on a special "A" frame by means of a Julius Suspension so that external vibrations are dampened.

Item D is the bath for the "cold junction" of the thermopile (secondary standard). It is a dewar containing a slurry of chipped distilled water ice and distilled water in about equal proportions. This bath must be stirred so that stratification can not set in; under these conditions the temperature will be 0.00° C.

Item E is the bath in which the comparison between the secondary standard and platinum resistance thermometer is made. It is a dewar holding a cylindrical copper block (L) about 4 in. in height in the top of which are wells 2 inches deep and containing mercury for immersion of the platinum resistance thermometer and the hot junction of the secondary standard. Since the required temperature range for the calibration is $61-65^\circ$ C., the dewar is filled with hot water at 65° C. or slightly above and is corked tightly.

Item F is the secondary standard. One junction F_c is immersed in the ice bath, the other F_h is immersed in the well of the copper block.

Item G is the platinum resistance thermometer. It has four leads, marked with the letters c, C, t, T, which are connected to the corresponding terminals on the G-2 bridge.

Item H is a standard cell, built to produce a constant, known e.m.f.

Item J is a suitable thermometer such as a Beckman for checking the temperature of the ice bath.

Item K is a two volt battery. The type used is a 3 cell storage battery, with the cells connected in parallel so that the e.m.f. across the terminals is two volts.

Since it is necessary to take readings on the K-2 potentiometer and G-2 Mueller bridge simultaneously, two people are needed to make the actual calibration. As the hot bath cools down from 65° C. to 61° C. readings on both instruments should be taken at the same instant, at ten or fifteen minute intervals, depending upon the cooling rate. Eight to ten sets of readings over this temperature range are considered ample for drawing the e.m.f.-temperature curve for the secondary standard.

It is presumed that the operation of the potentiometer and bridge is understood. For information concerning these see the Leeds and Northrup bulletins on "Type K Potentiometers Catalog E-50B (3)" and "Directions for No. 8069 Mueller Temperature Bridge".

To assure the accuracy of calibration the following precautions must be taken:

1. Readings on the K-2 potentiometer and the G-2 bridge must be taken at the same instant. If they are taken some seconds apart, it is likely that an error of 0.01° C. or more may be introduced depending upon the cooling rate of the hot water bath.

2. The ice bath must be at 0.00° C. throughout the run. It is well to check this temperature before calibration by measuring its temperature with the platinum resistance thermometer. The resistance of the

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platinum resistance thermometer in a bath of pure melting ice is given by the National Bureau of Standards calibration. The ice bath should be stirred and its temperature checked throughout the run with the Beckman thermometer.

3. It is essential that the G-2 bridge be at 35° C. and that the ratio, R_1 and R_0 dials be properly set. In addition, the zero for the bridge must be determined before each run. Directions for the settings and checks on the Mueller bridge are given in the bulletin mentioned above.

4. The potentiometer must be balanced against the standard cell before each reading. If this is not done the accuracy of the measurement may be doubtful.

IV. Calculation of Temperature of Platinum Resistance Thermometer

1. Correction of Bridge readings. - All readings on the G-2 bridge must be corrected according to the calibration of the bridge resistance coil by the National Bureau of Standards.

2. Platinum Resistance Thermometer Constants - The calculation of the temperature, equivalent to a given measured resistance of the platinum resistance thermometer, involves certain constants, the values for which must be determined for each platinum resistance thermometer. The constants for the platinum resistance thermometer, L and N No. 522049 NBS-742, were determined by the National Bureau of Standards and are as follows:

Resistance in melting ice (R_0) = 25.524 international ohms

Fundamental coefficient of the coil (c) = $\frac{R100 - R_0}{100 \ R_0}$ = 0.0039234

Constant in Callendar formula (δ) = 1.495

3. Formula and Calculation - The equation relating the temperature to the observed resistance of a thermohm is known as the Callendar formula and is

$$t = 100 \ \frac{R_t - R_o}{R_{100} - R_o} + \delta \left(\frac{t}{100} - 1\right) \frac{t}{100}$$

Where t = temperature $^\circ$C.

R_t = resistance of platinum resistance thermometer at temperature t

R_o = resistance at 0.00° C.

R_{100} = resistance at 100.0° C.

δ = 1.495

The Callendar formula may be written in another form which will simplify the calculation somewhat.

It is t = pt + correction

where $pt = 100 \ \dfrac{(R_t - R_o)}{(R_{100} - R_o)}$

Corr. = $\delta \left(\dfrac{t}{100} - 1\right) \dfrac{t}{100}$

But from the fundamental coefficient of the coil as given in the preceding section:

$$c = .0039234 = \frac{R_{100} - R_o}{100 \ R_o}$$

Then $R_{100} - R_o = 100 \ R_o \ (.0039234)$

$$= 100 \ (25.524)(.0039234)$$

$$= 10.01408$$

Substituting in $pt = 100 \ \dfrac{R_t - R_o}{(R_{100} - R_o)}$

$$pt = 100 \ \frac{(R_t - 25.524)}{(10.01408)}$$

$$pt = 9.98594 \ (R_t - 25.524)$$

By substituting the measured value of the resistance for R_t in the last expression, pt can be evaluated. Then by a method of approximation as follows t may be calculated.

If a value for the correction is assumed, t can be calculated from the expression t = pt $\neq$ correction. Then the assumed value for the correction is checked by substituting this value for t in

$$\text{corr} = \delta \left(\frac{t}{100} - 1\right) \frac{t}{100}$$

If this value for the correction checks the assumed one, the calculated value for t is correct and no further computation is needed. If, as is most likely, it does not check on the first assumption, assume the value for the correction just computed in the check calculation and recalculate t from t = pt $\neq$ correction. Then check the second assumption in the same manner as before. Repeat this process until the assumed value for the correction corresponds to the check result.

Sample Calculation

R_t = 32.0449

then pt = 9.9859 (32.045 - 25.524) = 65.117

First approximation

Assume correction of -0.340

then t = 65.117 - 0.340 = 64.777

Check of correction

$$\text{Corr} = \delta \left(\frac{t}{100} - 1\right) \frac{t}{100}$$

$$= 1.495 \left(\frac{64.777}{100} - 1\right) \frac{64.777}{100} = -0.341$$

This does not check the assumed correction, so another approximation
is needed.

Second Approximation

Assume correction = -0.341

t = 65.117 - 0.341 = 64.776

Check

$$corr = 1.495 \left(\frac{64.776}{100} - 1\right) \frac{64.776}{100} = -0.341$$

This checks the assumed value; then t = 64.776° C.

V. Plotting of Results

The calculated temperatures equivalent to each observed reading of the
e.m.f. of the secondary standard are plotted, temperature in °C. on the
abscissa and e.m.f. in microvolts on the ordinate. It is most convenient
to construct the graph on millimeter paper, with 0.1° C. per centimeter for
temperature and 50 microvolts per centimeter for the e.m.f. The resulting
plot should be nearly a straight line. If the points do not closely approxi-
mate a straight line, the calculations should be rechecked. If they are
correct, the calibration was inaccurate and should be repeated.

VI. Calibration of Thermopiles against the Secondary Standard

The method here employed is similar to that used in the calibration of
the secondary standard. The uncalibrated thermopile is calibrated against
the secondary standard thermopile by using two K-2 potentiometers and less
sensitive GE galvanometers may be used in place of the L&N galvanometers.
The set-up is diagrammed schematically in Figure 2.

The same care to insure accuracy as was observed in the calibration of
the secondary standard applies in this case. (See the section on precautions
above in the calibration of the secondary standard.)

No computations are necessary in this case. The bath temperature equivalent to the measured e.m.f. of the secondary standard is found from its e.m.f. temperature graph. The bath temperature thus found is the temperature corresponding to the observed e.m.f., at the give moment, of the thermopile being calibrated.

A plot is then made of the e.m.f. vs. temperature for the thermopile in the same fashion as it was made for the secondary standard. If the points do not follow a straight line, the calibration is in error and should be repeated.

More than one thermopile may be calibrated during the same run, if the copper block has the necessary number of wells. The different thermopiles can alternately be measured by the potentiometer circuit, by use of the proper switch arrangement. The e.m.f. of the secondary standard is read everytime the e.m.f. of each thermopile is read. If the thermopiles are in continual use it is advisable to recalibrate them monthly. Though the secondary standard is reserved for calibrations, it is advisable to recalibrate it against the platinum resistance thermometer every three months.

If the thermopiles are ever heated above the temperature at which they were annealed, they must be recalibrated.

SCHEMATIC DIAGRAM OF SETUP FOR CALIBRATING SECONDARY STANDARD

FIGURE 1
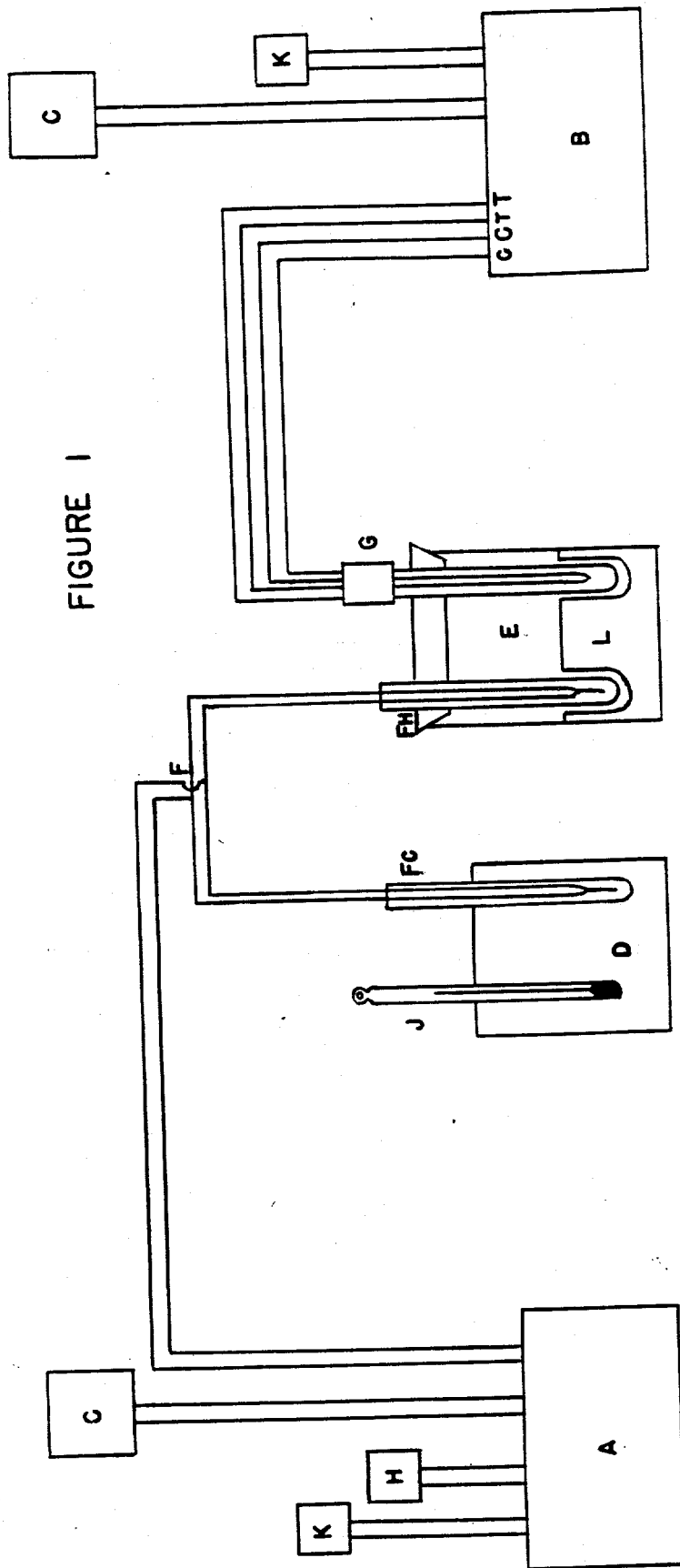
LEGEND

A - K2 POTENTIOMETER

B - G 2 BRIDGE

C - GALVANOMETER

D - ICE BATH

E - HOT BATH

F - SECONDARY STANDARD
FG & FH - COLD & HOT JUNCTIONS, RESPECTIVELY

G - PLATINUM RESISTANCE THERMOMETER

H - STANDARD CELL

J - BECKMANN THERMOMETER

K - BATTERIES

CCTT - BRIDGE TERMINALS FOR THERMOHM

L - BRASS BLOCK

2.1 B

SCHEMATIC DIAGRAM OF SETUP FOR CALIBRATING THERMOPILES AGAINST SECONDARY STANDARD

FIGURE 2

LEGEND

K - K2 POTENTIOMETER

S - STANDARD CELL

B - BATTERY (2 VOLT)

G - G.E. GALVANOMETER

H - HOT WATER BATH
(APPROX. 65°C. AT START OF RUN)

| - DISTILLED WATER ICEBATH AT 0°C.
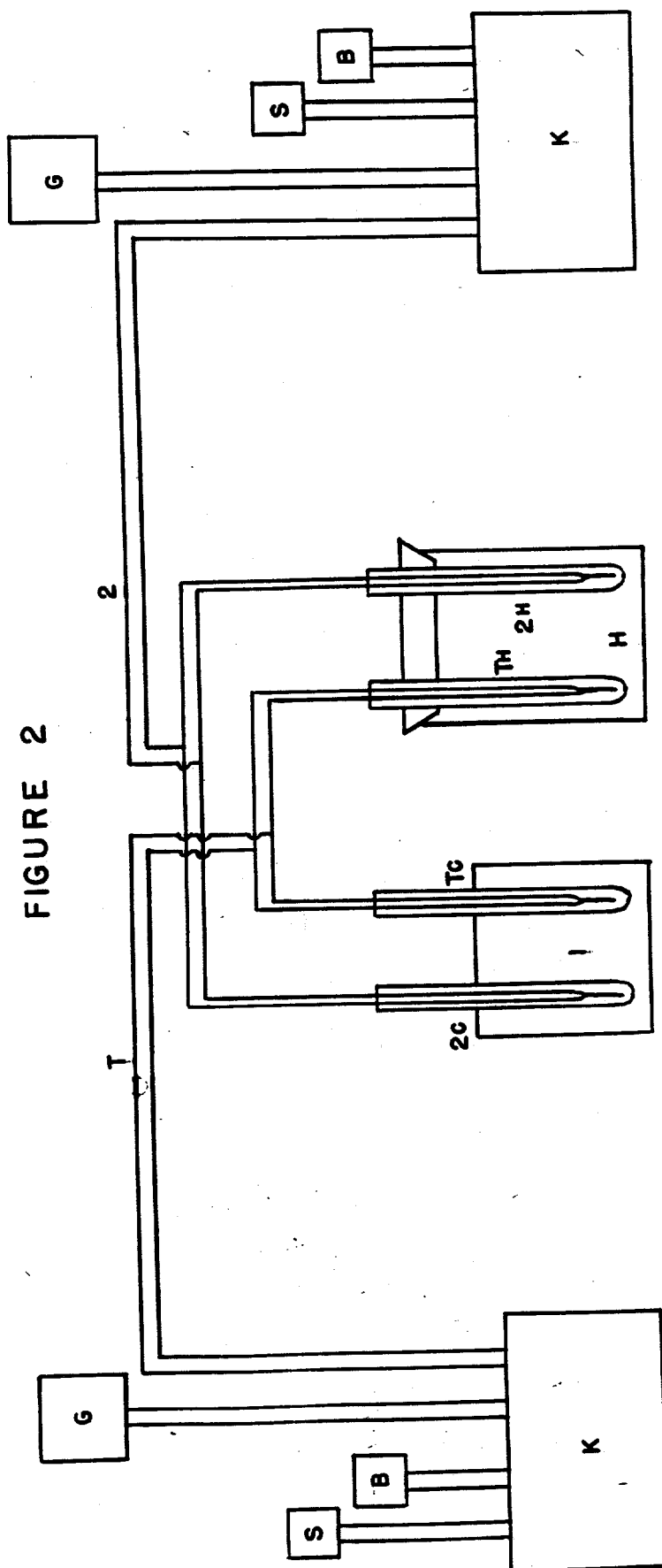
T - THERMOPILE
Tc - COLD JUNCTION
TH - HOT JUNCTION

2 - SECONDARY STANDARD
2c - COLD JUNCTION
2H - HOT JUNCTION

2.1 B

DETERMINATION OF HF IN C-616

By Freezing Point Method

The weight per cent of HF in a sample of C-616 is determined by measuring the lowering of the freezing point of the C-616.

A. Apparatus

1. Specially designed freezing point cell, referred to as Harshaw cell. See Figure 1.

2. Ten junction copper-constantan thermopile.

3. K-2 potentiometer.

4. General Electric galvanometer (Cat. 32 C).

5. Thermostatically controlled water bath.

6. Thermoregulators-calibrated for various bath temperatures.

7. Beckman thermometer.

8. Distilled water ice bath, with automatic stirrer.

B. Procedure

Operation	Reason for Operations
1. Heat Harshaw cell, containing sample, in an oven at 85° C. for 2-4 hours.	1. All C-616 must be liquefied to give an accurate freezing point run, since crystals or foreign particles prevent supercooling.
2. Prepare dewar containing mixture of distilled water and distilled water ice and place Beckman thermometer and one end of thermopile in the bath.	2. This bath is used to give a constant and reproducible temperature for one junction of the thermopile.

3. Check temperature of the hot bath. Always make first freezing point run at highest bath temperature 63.2 - 63.3° C.

3. The temperature of the bath should be slightly below that of the expected freezing point. Other thermoregulators are available which control the temperature at 62.4° C. and 61.6° C., and are used for samples of lower freezing point.

4. Place hot cell in water bath and pour about 1 ml. of bayoil in well.

4. The bayoil is used to produce good thermal contact between wall of well and thermopile.

5. Place thermopile in well, making sure that the lead wires are bent as little as possible. Make sure that the thermopile touches the bottom of the well.

5. The thermopiles should be handled with great care. They are delicate, and when damaged, impossible to repair. A great deal of time is required to construct and calibrate a new one. Care should also be taken to insure the correct thermopile goes into the right well.

6. Take the first reading of e.m.f. as soon as possible after the cell is placed in the bath.

6. If the reading is below 0.027000 volts the cell must be replaced in the oven and the run discontinued; the contents of the cell were not completely liquefied in that case.

7. Continue taking e.m.f. readings at 3 minute intervals as they drop with decrease in temperature. Record temperature of hot and cold baths at 10 minute intervals. Check standard cell reading periodically.

7. The cold bath temperature should remain absolutely constant, as shown by the Beckman thermometer. The hot bath should remain within $\pm 0.15^\circ$ C. of its original temperature.

8. When the C-616 has cooled below the expected freezing point, strike the cell with a rod. This should be done about 100 microvolts below the expected freezing point.

8. If the material has supercooled, the shock given the cell will induce freezing.

9. Obtain reading for freezing point at an e.m.f. value which remains constant over a period of about 10 minutes.

9. The time of the freezing point flat may vary, depending upon the purity of the material.

10. Determine freezing point temperature from a calibration curve.

11. Repeat the procedure for a check-run, using a different thermopile, if possible.

11. The freezing point values should check within the limits shown below.

C. Notes

1. There should be between 2-1/2 to 5 pounds C-616 in a Harshaw cell before a freezing point determination is begun. A cell containing less than 2-1/2 pounds of C-616 gives an unreliable freezing point, while one with more than 5 pounds is considered overloaded and dangerous to handle.

2. The accuracy of freezing point values decreases with a greater lowering of freezing point, as follows:

   a. $64.05 - 63.60^\circ$ C. $\leq 0.01^\circ$ C.

   b. $63.60 - 63.00^\circ$ C. $\leq 0.015^\circ$ C.

   c. $63.00 - 62.50^\circ$ C. $\leq 0.02^\circ$ C.

   d. $62.50 - 62.05^\circ$ C. $\leq 0.03^\circ$ C.

   e. 62.04° C. or less - not valid

3. Correct interpretation of freezing point runs is important, since not all samples exhibit definite supercooling and pronounced flats. The curve of a normal run is shown in Figure 3, with both supercooling and freezing definitely indicated. Instances of irregularities in freezing point runs are shown in succeeding figures. Figure 4 shows a run with no pronounced supercooling; Figure 5 illustrates an instance where there is definite supercooling but rather indefinite freezing point; Figure 6 represents a run with no apparent supercooling or freezing point.

In Figure 4, the freezing point flat is not preceded by a large temperature drop, but the actual freezing point may be considered as represented by the flat on the graph. The slight supercooling may be

due to foreign particles in the cell, or to an unintentional shock given the cell. If the flat is approximately 30-50 microvolts above the lowest point of the supercooling curve, the flat is considered valid.

In those cases illustrated by Figure 5, where supercooling is definite, but the flat uncertain, it is standard procedure to call the highest point of this section of the curve the freezing point.

If a sample behaves as shown in Figure 6, it is treated in one of two ways. First, if the hot bath regulator in use is not the lowest available, the cell is returned to the oven, reliquefied, and a subsequent run made using a lower bath regulator. Second, if the lowest hot bath regulator is in use, and no supercooling or freezing occurs, the material is considered to have a freezing point below the valid range. No re-run is made on this cell.

BRASS OR COPPER PIPE
2" LONG - THR. 1 END

SILVER SOLDER

KEROTEST
VALVE ° 7903

SILVER SOLDER

$\frac{3}{8}$" BRASS TEE

SILVER SOLDER

$\frac{3}{8}$"x2 BRASS NIPPLE

LITHARGE VISTANEX

NICKEL CYLINDER
APP CAPACITY - 765 CC
1.69" WATER

COPPER TUBE - 11" LONG APP.
.375 O.D - .311 I.D.

$7\frac{5}{10}$"

$\frac{1}{2}$"

$3\frac{5}{8}$"

$\frac{1}{8}$" THICK COPPER PLUG
SILVER SOLDERED
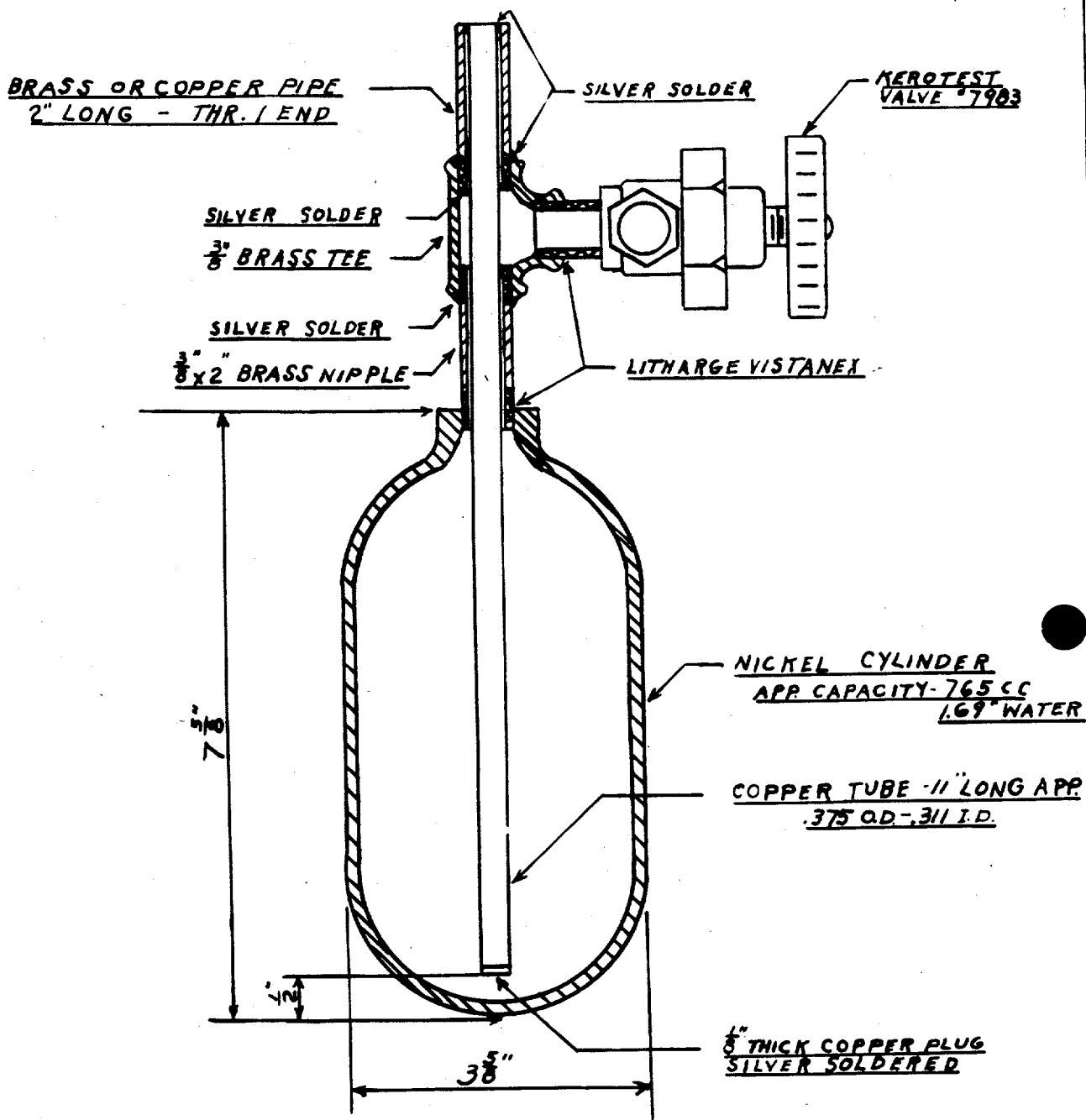
MODIFIED FREEZING POINT CELL

SCALE 6"=1'-0"

FIGURE 1

ASSEMBLY OF FREEZING POINT APPARATUS

FIGURE 2
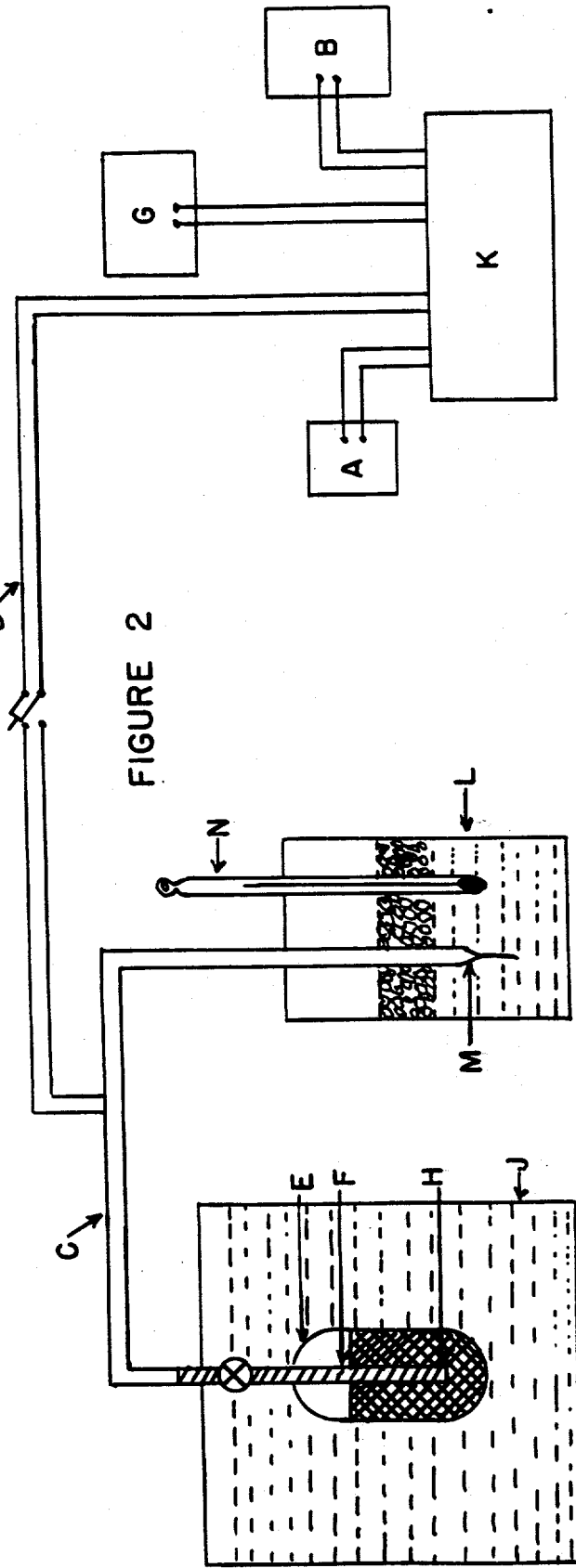
LEGEND

A - STANDARD CELL

B - STORAGE BATTERY

C - 10-JUNCTION THERMOPILE

D - LEADS FROM THERMOPILE

E - HARSHAW CELL

F - WELL IN HARSHAW CELL

G - G.E. GALVANOMETER

H - HOT JUNCTION OF THERMOPILE IN WELL

J - HOT BATH

K - K2 POTENTIOMETER

L - ICE BATH

M - COLD JUNCTION OF THERMOPILE

N - BECKMANN THERMOMETER

2.10

FIGURE 3

0.027500

0.027000

0.026500

E.M.F. IN VOLTS

F.P. FLAT AT 64.04°C

0.026000

63.20°C

HOT BATH TEMPERATURE = 63.20°C

TIME IN MINUTES

0   5   10   15   20   25   30

FIGURE 4

0.028000

0.027500

0.027000

E.M.F. IN VOLTS

0.026500

F.P. FLAT AT 64.03°C

63.65°C

HOT BATH TEMPERATURE = 63.20°C

0.026000

TIME IN MINUTES

0   5   10   15   20   25

2.10

FIGURE 5

0.026500

0.026000

0.025500

F.P. FLAT AT 62.08°C

HOT BATH TEMPERATURE = 61.80°C

EMF IN VOLTS

0.025000

TIME IN MINUTES

0   5   10   15   20   25   30

0.027000

FIGURE 6

0.026500

0.026000

0.025500

NO F.P. FLAT

NO SUPERCOOLING

F.P. < 62.04°C

EMF IN VOLTS

0.025000

HOT BATH TEMPERATURE = 61.80°C

TIME IN MINUTES

0.024600

0   5   10   15   20   25   30

PURGE GAS ANALYSIS

The purpose of this test is to determine whether the concentration of C-616 in a piece of equipment exceeds the safe limit. The safe limit has been set at a concentration of 10 parts per million. To run the test, the pressure in the equipment under test, must be greater than atmospheric.

A volume of gas is bubbled through water, and the water is tested for TO_2^{++} ion with potassium ferrocyanide. If the concentration of C-616 in the gas is greater than 10 ppm, a brown color is obtained. If the concentration of C-616 is less than 10 ppm, there is no change in color.

I. Apparatus

The apparatus used is shown in Figure 1.

II. Reagents

10 per cent Potassium Ferrocyanide

Dissolve 10 grams of $K_4Fe(CN)_6$ in 100 ml. of water. This solution should be made fresh every two weeks.

III. Procedure

A. Check to see that the pressure in the cell is above atmospheric and that the G-74 valve to the C-216 charging line is closed.

B. Attach the clamp to the flange on the C-216 charging line and open the valve to the cell. Attach the bubbler and purge the line for two minutes with the valve on the clamp wide open. Rinse out the bubbler with distilled water.

C. Fill the bubbler with 40 ml. of distilled water.

D. Bubble the gas through the water at the rate of 3 liters per minute for six minutes. (Do not allow the water to bubble over into the flow manometer).

E. After bubbling, dilute the solution to 100 ml. and pour some of the solution on a porcelain spot plate. Add a drop of potassium ferrocyanide to it. If a brown color forms, the concentration of C-616 in the gas was greater than 10 parts per million.

F. Report as "Positive - greater than 10 ppm" or "Negative - less than 10 ppm".

END VIEW OF C CLAMP

CAPILLARY FLOW METER MOUNTED ON END OF CARRYING BOX

RUBBER CONNECTOR

CONNECTION FOR PURGING LINE

C CLAMP

SLOT FOR RUBBER GASKET

BRASS HOKE NEEDLE VALVES

WATER

TUBE OF 100 ML CAPACITY

SINTERED GLASS BUBBLER

3/8" COPPER TUBING

FLANGE FOR C-216 CHARGING

CELL
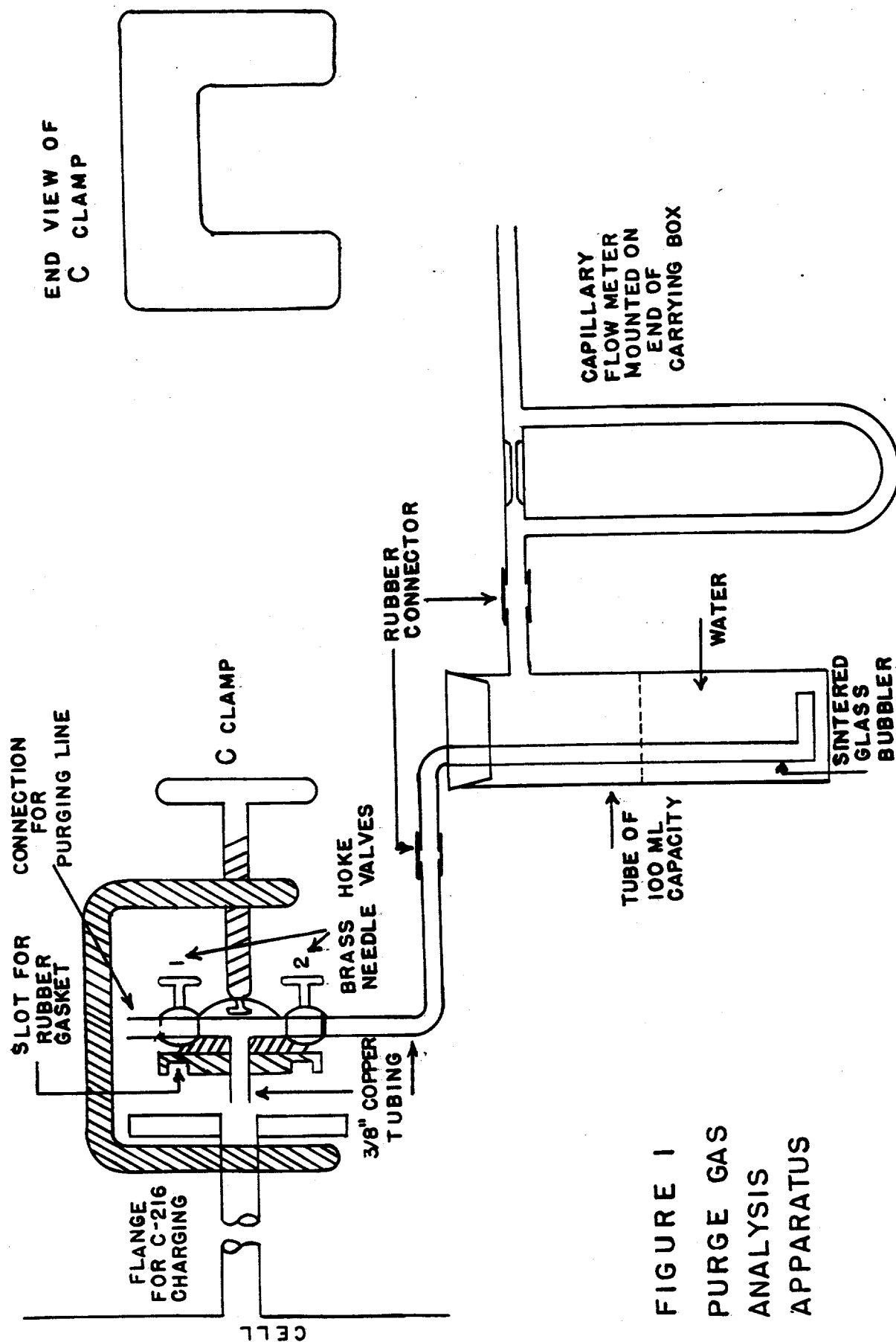
FIGURE 1

PURGE GAS ANALYSIS APPARATUS

2.2

DETERMINATION OF T IN C-616 ASSAY SAMPLES

Method:

The C-616 is hydrolyzed and converted to T sulfate by evaporation with sulfuric acid. It is then redissolved in dilute sulfuric acid, filtered and aliquoted to give a sample containing approximately 200 mg. of T. The T solution is then reduced in the Jones reductor. Trivalent T which is formed in the reduction is converted to tetravalent T by aerating the sample. The sample is then immediately titrated with ceric ammonium sulfate solution using ortho phenanthroline ferrous complex as indicator. The titration is best carried out by adding 1 or 2 ml. excess ceric ammonium sulfate solution and back-titrating the excess ceric sulfate with ferrous ammonium sulfate to a pink end-point.

Reagents and Apparatus:

1. Standard ceric ammonium sulfate solution - Dissolve sufficient ceric ammonium sulfate in 2 N sulfuric acid to give a 0.05 N ceric sulfate concentration. The solution should stand about two weeks and be filtered before standardizing.

2. Ferrous ammonium sulfate solution - Dissolve sufficient ferrous ammonium sulfate in 2 N sulfuric acid to make a 0.05 N solution.

3. Dilute sulfuric acid. (2 N)

4. Ortho phenanthroline indicator - Dissolve sufficient ortho-phenanthroline in 0.025 M ferrous sulfate to make the solution 0.075 M in ortho-phenanthroline. Warm to dissolve.

5. Jones Reductor: Prepare as described in Procedure 7.1.

Procedure:

A. Preparation of the sample:

1. Weigh the sample in the glass tube in which it is received. (See Figure 1).

2. Place the tube in a 300 ml. lipless beaker which contains about 5 cm. of distilled water.

3. Break the tube by pushing a pointed stirring rod through the thin glass face (A).

4. Add approximately 15 ml. of 6 N sulfuric acid and evaporate to SO_3 fumes on a hot plate.

5. Cool, and break the punctured sample tube about an inch from the rounded end. Put the rounded end in the beaker and wash the other end with the 2 N sulfuric acid. Discard the thoroughly washed end of the tube.

6. Add 10 ml. of 6 N sulfuric acid and again evaporate to fumes of SO_3.

7. Cool. Dissolve the material in 2 N sulfuric acid and filter into a volumetric flask. (If the weight of the sample is less than 1.8 grams filter into a 250 ml. volumetric flask. If it is more than 1.8 grams filter into a 500 ml. flask.)

8. Wash the paper with 2 N sulfuric acid and then make up to the mark with 2 N sulfuric acid.

9. Pipette sufficient solution to contain between 180 mg. and 360 mg. of T into a 150 ml. beaker.

Reduction of T:

1. Clean and activate the Jones reductor by passing 300 ml. of 2N sulfuric acid through it. Add about 200 ml. of water to displace the

acid in the reductor.

2. Carry out a blank titration as follows: Pass 150 ml. of 2 N sulfuric acid through the reductor followed by 200 ml. of water.

3. Determine the blank by adding 25-30 ml. of standard ceric ammonium sulfate, 2 drops of ortho-phenanthroline complex and titrate to a salmon pink end-point with ferrous ammonium sulfate solution.

4. Carry out a second cross titration as follows: Titrate 25-30 ml. of ceric ammonium sulfate solution in 150 ml. of 2 N sulfuric acid with the ferrous ammonium sulfate solution using 2 drops of ortho-phenanthroline complex indicator as before.

5. Calculate the cross-titer values obtained in (3) and (4) by dividing the volume of ceric ammonium sulfate used by the volume of ferrous ammonium sulfate and compare the values obtained. If the cross-titers do not check within 2 parts in 1000 repeat steps (3) and/or (4).

6. Reduce the sample as before. Pass 50 ml. of 1 N sulfuric acid through the reductor. Then pass the entire sample containing T through the reductor. Wash the beaker with two 25 ml. portions of 2 N sulfuric acid and pour the washings through the reductor. Wash the beaker with water and run the washings through reductor. Add sufficient water to bring total water wash to 100-150 ml.

7. Aerate the reduced sample for at least five minutes to converter trivalent T (olive green) to the tetravalent state.

Titration:

1. Add 3 drops of ortho-phenanthroline complex to the reduced and aerated sample. Add ceric ammonium sulfate until the color changes and then add about 1-2 ml. excess.

-4-

2. Back-titrate to a salmon pink end-point and with ferrous ammonium
    sulfate.

Calculation:

$$\frac{(A-B \times \text{cross titer}) \times Me \times N}{W} \times 100 = \text{percent T}$$

A   =   ml. of ceric ammonium sulfate used.

B   =   ml. of ferrous ammonium sulfate used.

Me =   milliequivalent weight of T (0.119).

N   =   normality of ceric ammonium sulfate solution

FIGURE 1
DIAGRAM OF GLASS SAMPLING TUBE

3.4
2.3

Standard $^{10}/_{30}$ Female Taper

121 — Taper Number

Joint - A

Constriction

121-4 — Tube Number

Approx. 8"

Indentation

A

Sample Bulb
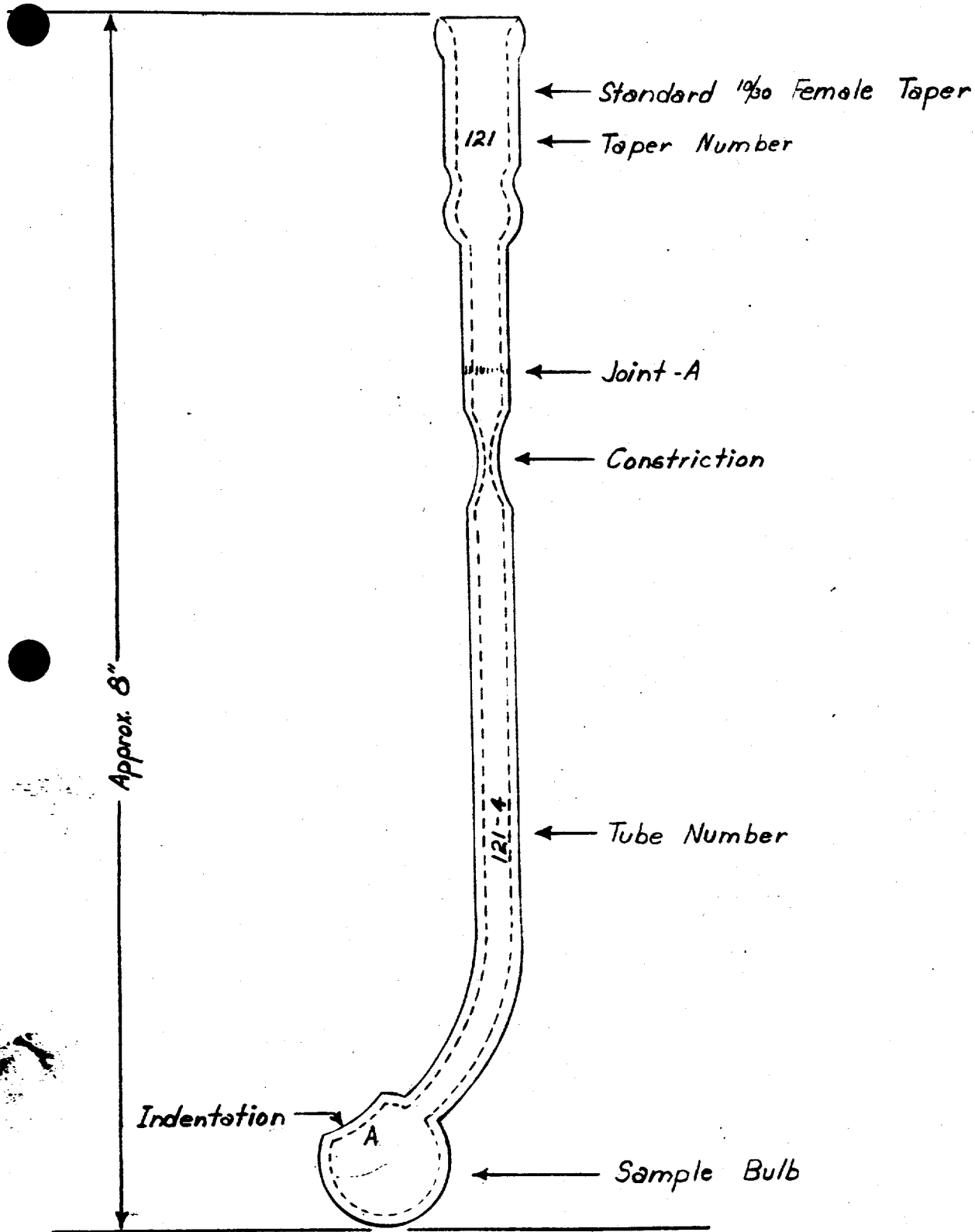
DETERMINATION OF C-616 IN G-74

Part B

Colorimetric Determination

This method is for the determination of C-616 in G-74. Part A includes directions for taking the gas sample into a 5 liter bulb; Part B includes directions for the solution of C-616 in water and the determination of the TO_2^{++} ion colorimetrically; Part C includes directions for the volumetric determination of the TO_2^{++} ion.

I. Apparatus

A. Sample Bulb - Five liter sample bulbs fitted with adapters as shown in Figure 1 are required. Cases are provided for the transportation of the bulbs.

B. Spectrophotometer - A Beckman Spectrophotometer is used for the determination of TO_2^{++} ion by the ferrocyanide method.

C. Photoelectric colorimeter - A Cenco Sheard-Sanford Photelometer is used for the determination of TO_2^{++} ion by the peroxide method.

D. Evacuating Manifold - Capable of evacuating 5 sample bulbs at one time. See Figure 2.

II. Reagents

A. Ferrocyanide Method

1. Formate Buffer - Dissolve 40 grams of reagent grade NaOH in 200 ml. of water. Add 46.1 ml. of 87% formic acid (Sp. Gr. 1.20) to this solution. Dilute the solution to 500 ml. with distilled water. Check the pH; it should be between 4.5 and 5.0.

2. Potassium Ferrocyanide - Dissolve 57.4 grams of analytical reagent grade $K_4Fe(CN)_6$ in 300 ml. of distilled water in a 500 ml. volumetric flask. After all the solid has been dissolved, dilute to the mark with distilled water. This solution should be made fresh every two weeks.

B. Peroxide Method

1. Sodium Peroxide - Tare (balance) a beaker containing about 300 ml. of water on a trip balance. Carefully add 25 grams of Parr Instrument Co. sodium peroxide (any calorific grade peroxide will be adequate for this use) with as little stirring as possible. Filter the solution through a medium porosity fritted glass crucible and dilute to 500 ml. The filtrate should be water white. When 15 ml. of the solution are diluted to 50 ml. with distilled water, the solution should have the same transmission as distilled water when measured in the Photelometer. This solution should be made fresh every seven days.

III. Procedure

A. Removal of solution from bulb

1. The sample will be received from the Process Area in a 5 liter bulb (See Figure 1) in a wooden case. Enter the information on the tag in the log book in the space provided. Give the sample a laboratory number. This number is to be written on the tag.

2. Add 1 ml. of conc. H_2SO_4 to 250 ml. of distilled water. Mix thoroughly. Suck 50 ml. of this solution into the bulb and shake

until all of the mist is dissolved. Open the stopcock and allow the bulb to come to atmospheric pressure. Remove the adapter from the bulb and pour the solution into a clean 250 ml. volumetric flask (use a clean funnel). Rinse the bulb with three more 50 ml. portions of acidified water. Dilute to mark with distilled water. Wash a clean bottle with three small portions of the solution, discard the washings, and transfer the remainder of the solution to the bottle. Transfer the sample tag from the bulb to the bottle.

NOTE: In some cases the amount of C-616 in the bulb will be so small that it will be necessary to evaporate the entire solution to dryness. These samples will be marked EVAP. in red on the tag.

B. Preparation of Bulbs for Re-use

1. Wash the ground glass surfaces on bulb and adapter with carbon tetrachloride (or trichlorethylene). Make sure that the stopcock is tied to the adapter. Rinse the bulb and adapter three times with distilled water and twice with acetone.

2. Place the bulb in the special drying oven for at least one half an hour. During half of this time dry air should be flowing into the bulb.

3. Remove the bulbs from the oven, grease stopcocks and ground glass joints with PFI grease and fit adapter to bulb while the bulb is still hot. The joints should have enough grease so that there will be no streaks, but not so much that grease will get into the bulb.

4. Grease the ball joint with IFI grease and attach bulb to special evacuation line (see Figure 2). Five bulbs may be purged at one time. Close valves 1 and 8, open valve 7 and any of valves 2-6 to which bulbs are attached. Open the stopcocks on the bulbs. Turn on the pump and be sure that both pumps are operating. Open valve 8. Allow the bulbs to be pumped until manometer reading is within 5 mm. or less of the day's corrected barometric pressure. The corrected barometric pressure for the day is found on chart in Room 15. Close valve 7 and watch the manometer several minutes. If there is no change in the manometer reading continue with 5. However, if the manometer indicates a leak, turn off valves 2-6 one at a time until the leak stops. Regrease the ground joints in the leaking bulb, pump the system and test for leaks again. Repeat until all the bulbs are tight.

5. Open valve 1 and allow dry C-74 to flow into the bulbs until the manometer shows a pressure 20 mm. above atmospheric.

6. Close valve 1, open valve 7, and once again pump to a vacuum of 5 mm. or less. Again close valve 7 and test the system for leaks by watching the manometer for several minutes. Open valve 1 and allow the pressure in the bulbs to come to 20 mm. above the atmospheric pressure. Close stopcock on bulbs. Remove the bulbs from the line and place in carrying cases.

C. Determination of TO_2^{++} ion in solution

In order to determine which method of analysis is to be used, carry out the following test. If the solution is definitely yellow,

analyze by the peroxide method. If there is any doubt as to the color of the solution, take one drop on a spot plate and add one drop of sodium peroxide reagent. If a distinct yellow color is produced, analyze by the peroxide method. Otherwise, analyze by ferrocyanide method.

1. Peroxide Method - (a) Rinse a 25 ml. pipette with distilled water, allow to drain thoroughly, and then rinse with several small portions of the solution to be analyzed. From the pipette measure a 25 ml. portion of the solution into a 50 ml. volumetric flask, add 15 ml. of sodium peroxide from a graduated cylinder and dilute the solution to the mark with distilled water. Mix the solution thoroughly.

(b) Rinse the Photelometer cell several times with small portions of the solution and then fill the cell with the solution. Dry outside of cell thoroughly with lens paper and measure its transmission at 410 millimicrons (Filter A) against distilled water with the Photelometer.

(c) If the transmission reads less than 12% the sample must be rerun with a smaller aliquot. Rinse a 10 ml. pipette with distilled water, allow to drain thoroughly and then rinse with several small portions of the solution to be analyzed. From the pipette measure a 10 ml. portion of the solution into a 50 ml. volumetric flask, add about 10 ml. of distilled water and 15 ml. of sodium peroxide from a graduated cylinder and dilute the solution to

the mark with distilled water. Mix the solution thoroughly and read its transmission at 410 millimicrons with the Photelometer as outlined above. If the transmission of this sample is less than 12% a 1 ml. aliquot must be used.

(d) From the same pipette used to obtain the 10 ml. sample measure 10 ml. of the solution into a 100 ml. volumetric flask and dilute to the mark with distilled water. Rinse the 10 ml. pipette with distilled water and then several small portions of the dilute solution. From the pipette measure 10 ml. of the diluted solution into a 50 ml. volumetric flask. Add about 10 ml. of distilled water and 15 ml. of sodium peroxide solution. Dilute to the mark with distilled water. Mix thoroughly and read the transmission at 410 millimicrons with the Photelometer as outlined above.

(e) The transmission used for the determination of the amount of C-616 in the water should be between 70% and 12%. From the per cent transmission determine the mg. T present in the aliquot by means of Figure 3. Record the per cent transmission and amount of aliquot in the log book.

2. Ferrocyanide Method

If the solution is not yellow and does not give a yellow spot test with sodium peroxide solution, use the following method: (a) rinse a 50 ml. pipette with distilled water and then rinse with several portions of the solution to be analyzed. Save the washings for recovery in bottles provided. By means of the pipette, transfer

50 ml. of the solution from the bottle to a platinum dish. (If a platinum dish is not available, a 400 ml. Pyrex beaker may be used).

(b) Add 3 ml. of conc. H_2SO_4 and evaporate to dryness on on electric hot plate, using asbestos sheet thick enough to prevent active boiling.

(c) Add 3 more ml. of conc. H_2SO_4. If the residue at this point is brown or black also add 5 to 10 drops perchloric acid. Evaporate the solution to dryness once more on the hot plate. If perchloric acid has been added to the solution, add 3 more ml. of H_2SO_4 and evaporate to dryness a third time.

(d) Dissolve the residue in distilled water and transfer to a 50 ml. volumetric flask. Wash the dish with several portions of distilled water and filter through quantitative filter paper (Whatman's 42 or 44) into the 50 ml. volumetric flask. Wash filter paper with several small portions of distilled water and dilute to the mark with distilled water.

(e) Rinse a 25 ml. pipette with distilled water, drain, and rinse with two small (not over 1 ml. each) portions of the solution. Transfer 25 ml. of the solution to a 50 ml. volumetric flask by means of the pipette. Add 10 ml. of distilled water from a burette and then 4 ml. of the formate buffer and 10 ml. of the ferrocyanide. Dilute to the mark with distilled water.

(f) Prepare a solution containing 4 ml. of buffer and 10 ml. of ferrocyanide in a 50 ml. volumetric flask and dilute to the mark with distilled water. This solution is to be used as a standard.

(g) Fill one 10 cm. spectrophotometer cell with the unknown solution and another with the standard. Rinse the spectrophotometer cell several times with the solution used in it before filling. Dry the outside of the cell carefully with lens tissue before measuring the transmission.

(h) Measure the transmission of the unknown solution against the standard (prepared in f) using the Beckman Spectrophotometer at a wave length of 525 millimicrons. Use the cells having a 10 cm. solution depth. (Note: Before use, the cells should both be filled with distilled water and the transmission measured. If the transmission of the cells is not the same, they should be thoroughly cleaned with trisodium phosphate, rinsed and the transmission measured again).

(i) If the transmission of the sample is less than 30% the procedure should be repeated using a 10 ml. aliquot. Rinse a 10 ml. pipette with two small (not over 1 ml.) portions of the solution in the 50 ml. volumetric flask. Pipette 10 ml. of this solution to a 50 ml. volumetric flask. Add 25 ml. of distilled water, 4 ml. of the formate buffer and 10 ml. of the ferrocyanide. Dilute to the mark with distilled water. Measure the transmission of this solution against the standard solution in the manner outlined above.

(j) If the transmission of the sample is less than 30% the sample is rerun using a 1 ml. aliquot. Measure 10 ml. of solution from the same 10 ml. pipette used above into a 100 ml.

volumetric flask. Dilute to the mark with distilled water. Rinse the 10 ml. pipette with distilled water and several small portions of the diluted solution. Measure 10 ml. of the solution from the pipette into a 50 ml. volumetric flask. Add 25 ml. of distilled water, 4 ml. of formate buffer and 10 ml. of ferrocyanide. Dilute to the mark with distilled water. Measure the transmission of the solution against the standard as outlined above.

(k) The final transmission of the sample should be between 90% and 30%. If the transmission of the 1 ml. sample is less than 30% the sample should be rerun using the Peroxide method. (This will not happen if the spot test has been properly carried out). Record per cent transmission and aliquot in log book. From the per cent transmission of the sample determine the mg. T in the aliquot from a curve similar to Figure 4. (Figure 4 will vary with different lots of ferrocyanide; therefore, it is necessary that the curve be checked with solutions containing known amounts of TO_2^{++} ion from time to time.)

NOTES:

(1) Samples which come from the Process Area with the mark EVAP. in red on the tag should receive the following treatment:

Extract the sample from the bulb in the usual way, but collect it in a 400 ml. beaker rather than a volumetric flask. Add 3-4 ml. of conc. H_2SO_4 and evaporate to dryness on an electric hot plate, using asbestos sheets to control rate of evaporation. Add 3 ml.

more of conc. H_2SO_4. If the residue at this point is brown or black also add 5-10 drops perchloric acid. Evaporate the solution to dryness once more on the hot plate. If perchloric acid has been added to the solution, add 3 ml. more H_2SO_4 and evaporate to dryness a third time.

Dissolve the residue in 15 ml. of distilled water and filter through quantitative filter paper (Whatman's 42 or 44) into a 50 ml. volumetric flask. Wash the beaker and filter paper with four 5 ml. portions of distilled water. Add the washings to the original solutions. Add 4 ml. of the formate buffer and 10 ml. of ferrocyanide and dilute to the mark with distilled water.

Measure the transmission in the usual way with the spectrophotometer.

(2) Samples which are found to contain greater than 50 mol. per cent C-616 should be run volumetrically by the method outlined in Part C.

IV. Calculations

From Figure 3 or 4 determine the mg. T in the aliquot.

(1) $\text{Mg. T in aliquot} \dfrac{250}{\text{ml. of aliquot}} = \text{total mg. T in sample}$

(2) $\dfrac{\text{Total mg. T}}{238} = \text{millimols T}$

(3) $\text{Vol. of bulb (in ml.)} \dfrac{(P)}{(760)} \dfrac{(273)}{(273 + t)} = \text{Vol. of gas at}$

STP (ml.)

$P = \text{Pressure in mm.}$ $t = \text{temperature in } °C.$

(4) $\dfrac{\text{Vol. of gas STP (in ml.)}}{22.4}$ = millimols gas

(5) $\dfrac{\text{Millimols T} \times 100}{\text{Millimols gas}}$ = mol. % C-616 in gas

Combining to one equation

(6) Mol. % C-616 in gas = $\dfrac{(\text{Mg. T in aliquot})(273+t)(250)(22.4)(760)(100)}{(\text{vol. of bulb})(P)(\text{ml. aliquot})(273)(238)}$

Combining all constants

(7) Mol % C-616 = $\dfrac{(\text{Mg. T in aliquot})(273+T)(6550)}{(\text{vol. of bulb})(P)(\text{ml. aliquot})}$

If total sample is analyzed

(8) Mol. % C-616 = $\dfrac{(\text{Total mg. T})(273+t)(26.2)}{(\text{volume of bulb})(P)}$

If sample is analyzed by the ferrocyanide method, the entire sample evaporated to dryness and had a transmission of greater than 90%, calculate the result as though the transmission read 90% and report the sample as <u>less than</u> the calculated value. If the sample is analyzed by the ferrocyanide method and the 25 ml. aliquot has a transmission greater than 90%, evaporate a 150 ml. portion of the sample to dryness and run the determination on the evaporated solution in the same way the solutions marked EVAP. are run. If the transmission is still greater than 90%, follow the procedure outlined above. <u>Report only two significant figures.</u>

Table 1 shows the approximate range of both methods on the assumption that the volume of the sample is 5 l., the pressure 150 mm, and the temperature 30° C. This table will serve as a guide to what can be expected from the method.

In some cases there may be a question as to the chance of condensation of C-616 in the bulb. By referring to Figure 5 one may determine whether condensation will take place. Use this graph in the following manner. Follow the temperature line which is closest to the temperature of the bulb until it intersects the pressure of the bulb (on horizontal axis). The mol. % of C-616 shown on the vertical axis at this point is the maximum amount of C-616 which can exist in the bulb without condensation at this temperature and pressure. If the mol per cent C-616 found is greater than this value, report that the value is greater than the value indicated on the curve.

TABLE I

LIMITS OF T N LYSIS

All calculations are based on sample taken in 5 liter bulb at 150

mm. and 30° C. (Corr. Vol. = 900 ml.)

Ferrocyanide Method

Dilution of Sample (ml.)	Aliquot (ml.)	Minimum Vol. % C-616	Maximum Vol. % C-616	Range (mg.T) Min.	Max.
Evaporate to Dryness	Dilute sample to 50 ml.	3×10^{-4}	0.005	0.03	0.47
250	25	0.003	0.05	0.3	4.7
250	10	0.008	0.13	0.75	11.80
250	1	0.08	1.3	7.5	118.0

Peroxide Method

250	25	0.52	5.8	50	550
250	10	1.3	11.8	125	1,375
250	1	13.0	118.0	1,250	13,750

TAPERED STOPPER
24/40 FEMALE

4MM STRAIGHT
BORE STOPCOCK

TAPERED STOPPER
24/40 MALE

BALL JOINT
18/9 MALE

A ADAPTER FOR
SAMPLING BULB

5-LITER BULB
ROUND BOTTOM

B SAMPLING BULB
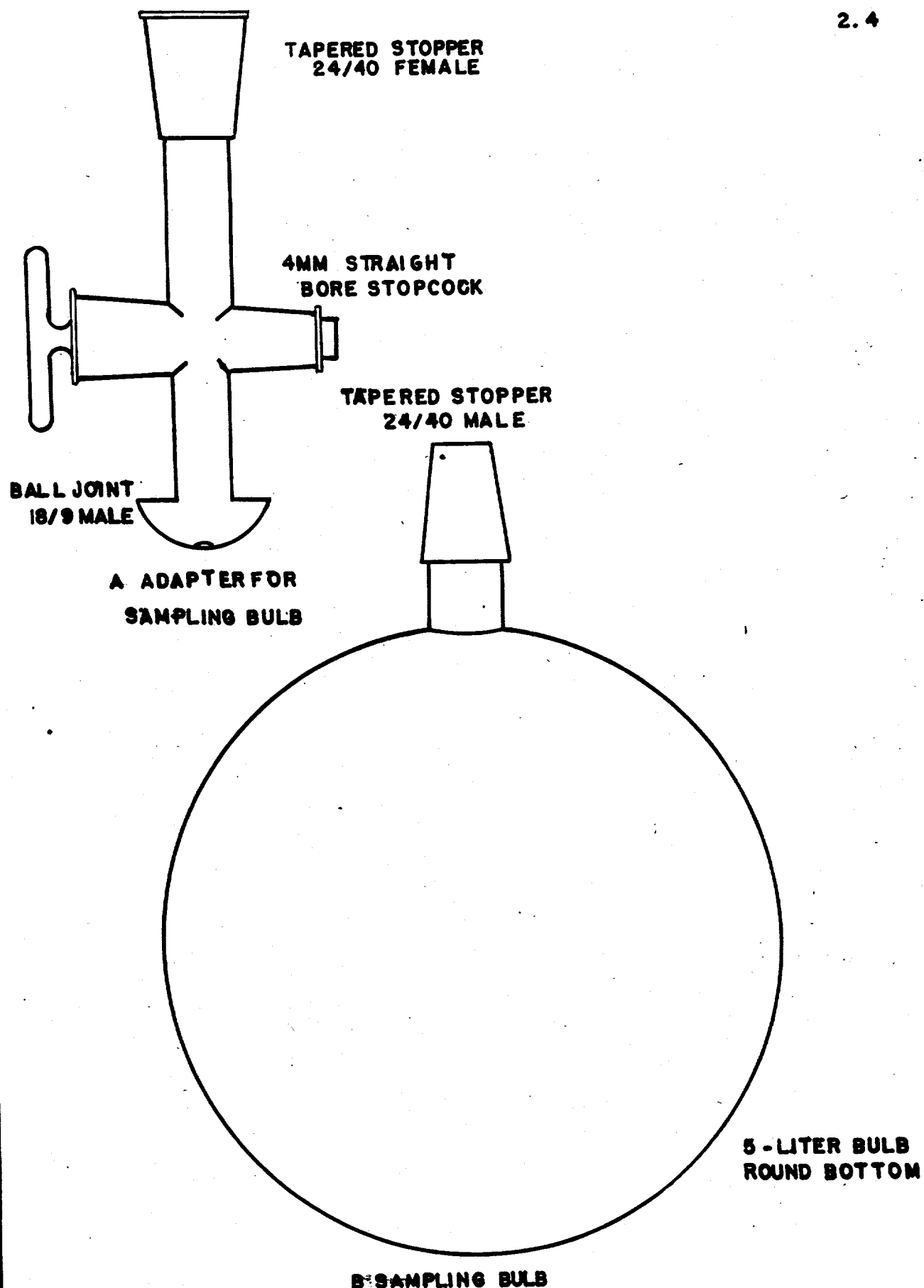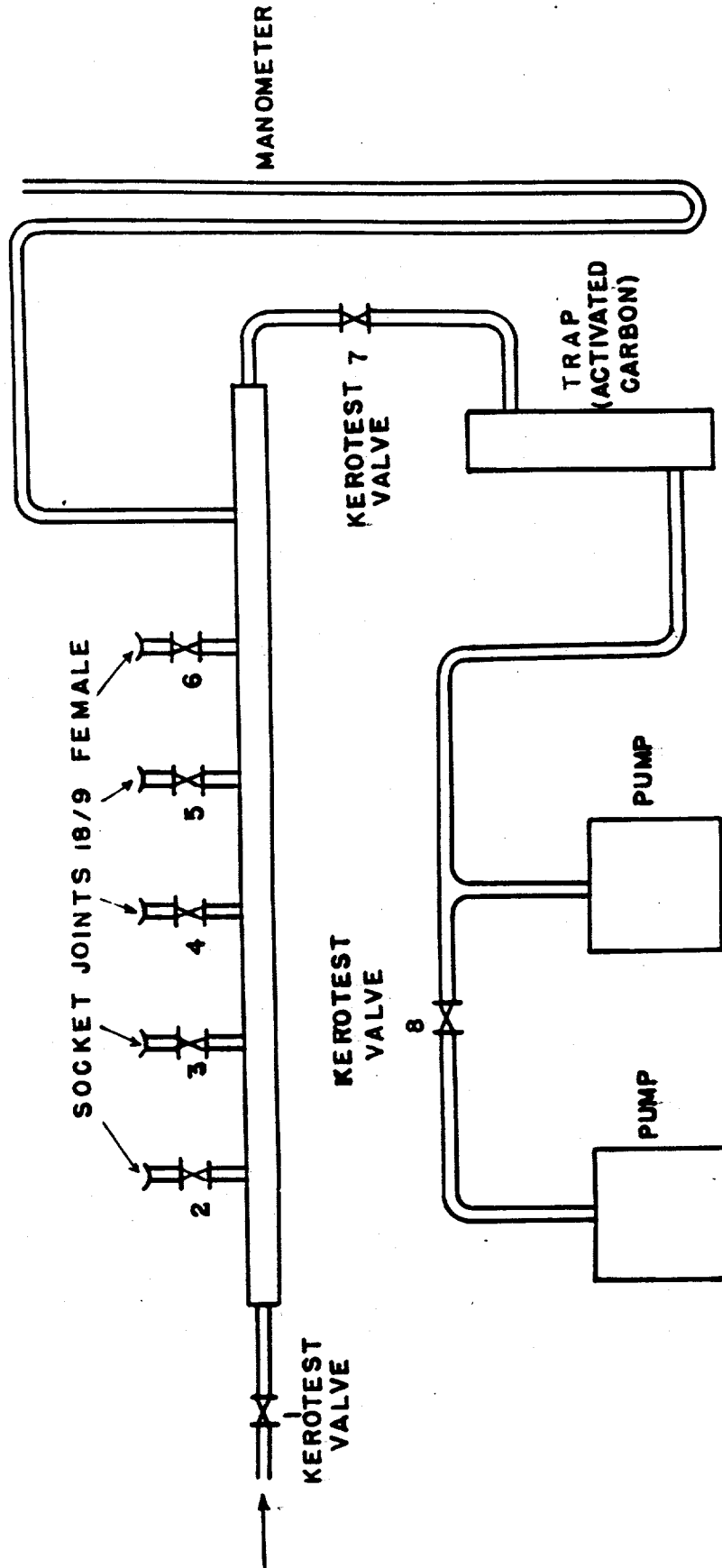
FIGURE I

PUMPING MANIFOLD

FIGURE 2
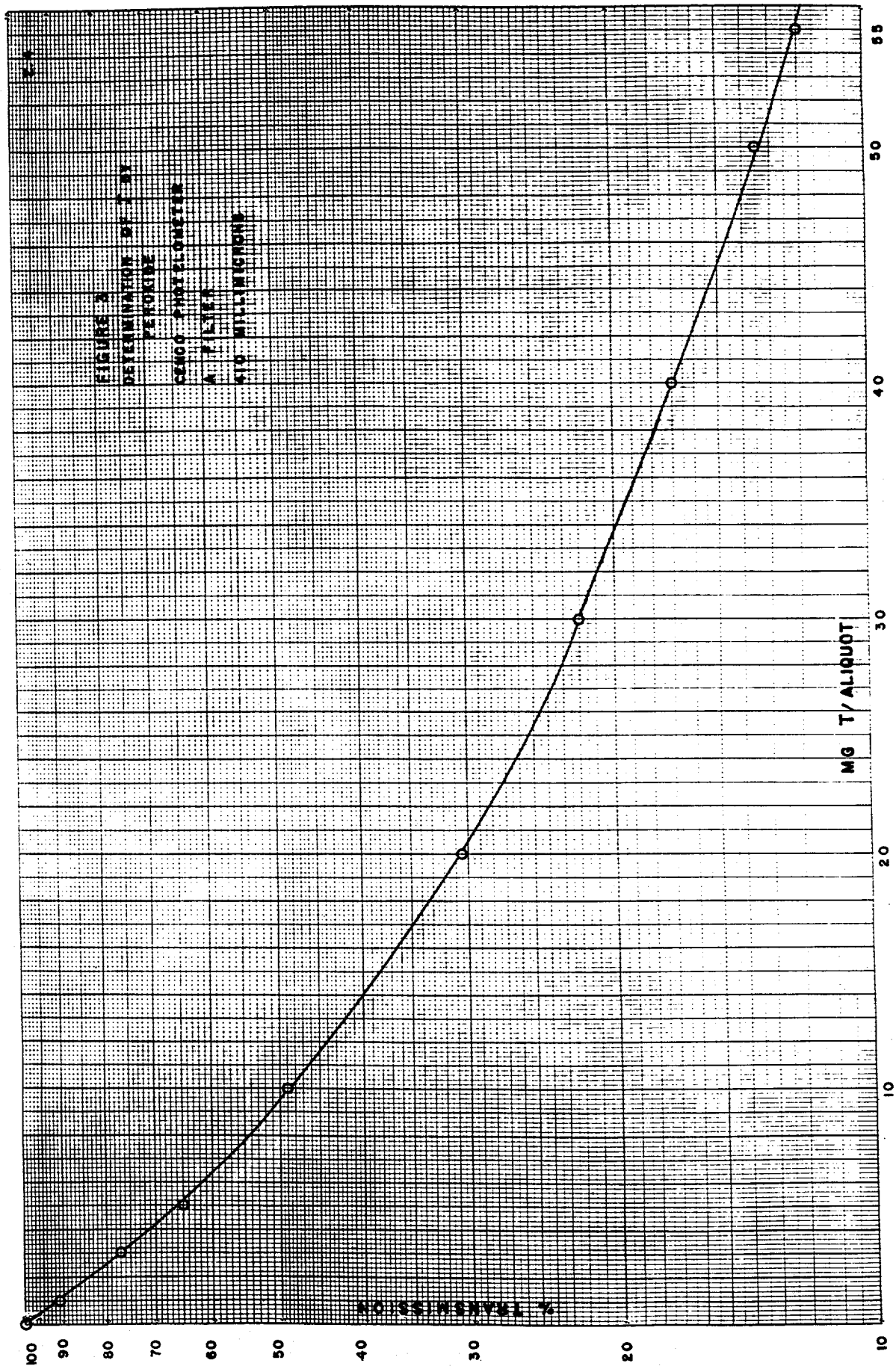
FIGURE 3

DETERMINATION OF P_2O_5 BY
AEROXIDE

CENCO PHOTELOMETER
#1 FILTER
410 MILLIMICRONS

% TRANSMISSION

MG T/ ALIQUOT

FIGURE 4
DETERMINATION OF T BY
FERROCYANIDE
BECKMAN SPECTROPHOTOMETER
10 CM. CELLS
525 MILLIMICRONS

Figure 4

COMBUSTION LIMIT OF C-616 AT DIFFERENT TEMPERATURES/PRESSURES

Maximum Mol % C-616

MAXIMUM MOL % OF C-616

PRESSURE IN BULB (mm.)

HRB 9-12-65

-1-
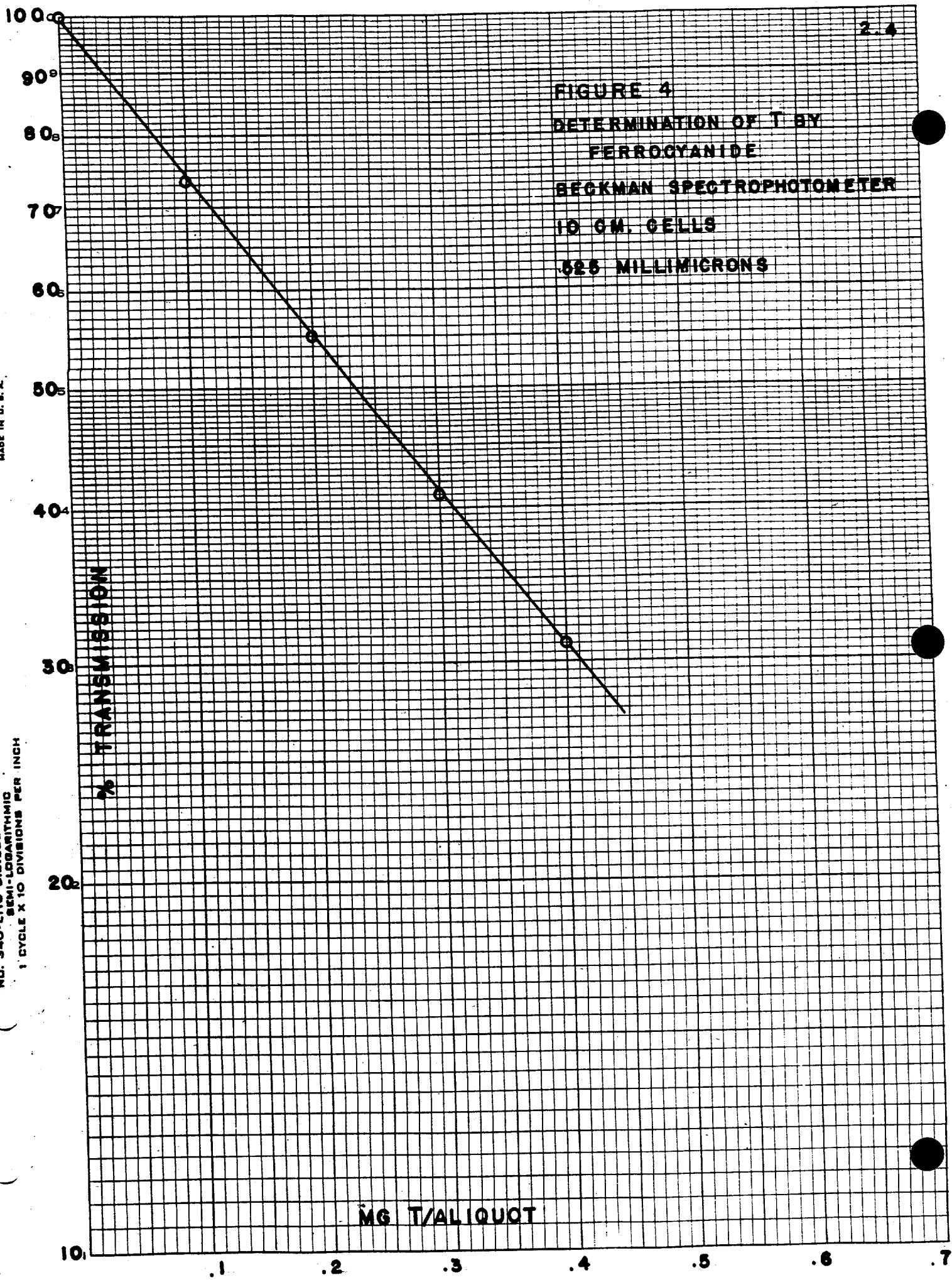
DETERMINATION OF C-616 IN G-74

Part C

Volumetric Determination

This method is for the determination of C-616 in G-74. Part A
includes directions for taking the gas sample into a 5 liter bulb;
Part B includes directions for the solution of C-616 in water and the
determination of the TO_2^{++} ion colorimetrically; Part C includes
directions for the volumetric determination of the TO_2^{++} ion.

I. Apparatus

A. Jones Reductor - The usual form of the Jones reductor is used.
Care must be taken that the reductor is always kept full of water
when not in use.

II. Reagents

A. Amalgam for Jones Reductor - To 100 grams of 20-30 mesh zinc add
100-150 ml. of 2% mercuric chloride and mix well. Wash with distilled
water until washings are clear. Do not expose to air.

B. 2% Mercuric Chloride - Dissolve 3 grams of $HgCl_2$ in 150 ml. of
distilled water.

C. 1:20 Sulfuric Acid - To 900 ml. of distilled water add slowly 45
ml. of conc. sulfuric acid.

D. 1 N Ferric Ammonium Sulfate - Dissolve 482.19 grams of NH_4 Fe
$(SO_4).12 H_2O$ in distilled water and dilute to 1 liter.

E. 0.100 N Potassium Dichromate - Dissolve 4.904 grams of dried
analytical reagent grade $K_2Cr_2O_7$ in water and dilute to 1 liter in a
volumetric flask.

F. Diphenylamine Sulfonic Acid - Dissolve 0.32 grams of barium di-
phenylamine sulfonate in 100 ml. of distilled water and 1 ml. conc.

sulfuric acid. Allow precipitate to settle and decant. Use the clear liquid.

III. Procedure

A. Run a blank with the reductor in the following manner:

1. Pass 100 ml. of 1:20 H_2SO_4 through the reductor and follow this with 100 ml. of distilled water.

2. Aspirate air through the sample for ten minutes.

3. Add 5 ml. of ferric ammonium sulfate and 1 ml. of diphenylamine sulfonic acid indicator. Titrate the solution with 0.100 N potassium dichromate added from a micro burette until 1 drop turns the solution purple. This titration is the blank for the reductor and should not be greater than 0.2 ml. If the blank is greater than this, wash the reductor with 200-300 ml. of 1:20 H_2SO_4 and repeat the blank.

B. Determination

1. Pipette an aliquot containing 40-80 milligrams of T into a clean beaker. (The amount of aliquot to be added may be determined from results in Part B.).

2. Add 100 ml. of 1:20 H_2SO_4 and pour the solution slowly through the Jones reductor.

3. Wash the beaker and reductor with 100 ml. of distilled water.

4. Aspirate air through the sample for ten minutes.

5. Add 5 ml. of ferric ammonium sulfate solution and 1 ml. of diphenylamine sulfonic acid indicator.

6. Titrate to the appearance of a purple color with 0.100 N potassium dichromate added from a micro burette.

IV. Calculations

(ml. $K_2Cr_2O_7$ for sample - ml. $K_2Cr_2O_7$ for blank) = net ml. $K_2Cr_2O_7$

(net ml. $K_2Cr_2O_7$) (11.9) = mg. T/aliquot

From the amount of T found in the aliquot, the mol per cent of C-616 in the bulb can be calculated by the equations given in Part B.

DETERMINATION OF F.C. IN C-416

I. Operating Procedure

1. Connect plugs (a, b, and c) to motor, globar, and galvanometer of the gas analyzer. See Figure 1.

2. Adjust the variac connected to the globar source between 35 and 40 volts. While the globar is operating, keep it water cooled.

3. Connect the 6 volt storage battery to the exciter lamp. Rotate batteries every day.

4. Keep the stopcock between the two detectors open except when taking readings. See Figure 3. Shield the detector unit from drafts and strong heat sources.

5. The deobase drop in the capillary tube should be between 6 and 7 units on the scale in the detector unit. Adjust the drop by opening the stopcock and leveling the detector by means of the leveling screws. See Figure 3.

II. Determining Dead Zone at Balance Point

1. Place an evacuated absorption cell in the gas analyzer.

2. Turn the shutter knob until shutter is open (Figure 2).

3. Close the stopcock (Figure 3) and turn the galvanometer control knob to 1/4.

4. Read the deflection on the galvanometer and record the results.

5. Open the stopcock (Figure 3) and turn off the galvanometer control.

6. Turn the shutter knob (Figure 2) counter-clockwise by quarter turns and by following steps 2, 3, and 4, record galvanometer deflections until the deflection is zero or begins increasing greater than the previous reading. This is the zero point.

7. After reaching the zero point, turn the shutter knob clockwise until a deflection of 20 to 30 mm. on the galvanometer is read for the evacuated absorption cell. The shutter opening will remain the same for all sample readings while the absorption cell is used.

III. Analytical Procedure

1. Check the instrument to be sure it is in operating condition.

2. Evacuate the absorption cell in the transfer system, and after evacuation, place in the gas analyzer, close detector stopcock, turn the galvanometer control switch to 1/4, allow time for 4 or 5 galvanometer deflections, and record 5 deflections of the galvanometer readings to within the nearest half millimeter.

3. Open the detector stopcock and close the galvanometer control switch.

4. Average the results to give the vacuum deflection.

5. Transfer pure C-616 to the absorption cell in the transfer system to 8 cm. Hg pressure.

6. Place the absorption cell containing the standard or pure C-616 in the gas analyzer, close the detector stopcock, turn the galvanometer control switch to 1/4, and after allowing time for 4 or 5 deflections, record 5 deflections of the galvanometer.

7. Open the detector stopcock, turn off the galvanometer control switch, and evacuate the absorption cell in the transfer system.

8. Average the deflection readings to give standard deflection.

9. Repeat Steps 5 through 8 with the sample of C-616 to be analyzed to get sample deflection.

IV. Method of Calculation

$$\frac{\text{Vacuum deflection} \neq \text{sample deflection}}{\text{Vacuum deflection} \neq \text{standard deflection}} = \text{ratio}$$

Referring to chart, the per cent FC can be found.

V. Sample Calculation

Vacuum deflection   -   25.0 mm.

Standard deflection -   31.0 mm.

Sample deflection   --   40.6 mm.

$$\frac{25.0 \neq 40.6}{25.0 \neq 31.0} = \frac{65.6}{56.0} = 1.16$$

From the chart, when ratio is 1.16, the per cent FC is 0.014.

CHART FOR DETERMINING % FC

Ratio of Deflect	% FC	Ratio of Deflect	% FC	Ratio of Deflect	% FC	Ratio of Deflect	% FC	Ratio of Deflect	% FC	Ratio of Deflect	% FC
1.00	0.000	1.21	0.018	1.42	0.036	1.63	0.058	1.84	0.082	2.05	0.108
1.01	0.001	1.22	0.019	1.43	0.037	1.64	0.059	1.85	0.083	2.06	0.109
1.02	0.002	1.23	0.019	1.44	0.038	1.65	0.060	1.86	0.084	2.07	0.110
1.03	0.003	1.24	0.020	1.45	0.039	1.66	0.061	1.87	0.085	2.08	0.111
1.04	0.004	1.25	0.021	1.46	0.040	1.67	0.062	1.88	0.087	2.09	0.112
1.05	0.005	1.26	0.022	1.47	0.041	1.68	0.063	1.89	0.088	2.10	0.113
1.06	0.005	1.27	0.023	1.48	0.042	1.69	0.064	1.90	0.089	2.11	0.114
1.07	0.006	1.28	0.024	1.49	0.043	1.70	0.065	1.91	0.090	2.12	0.115
1.08	0.007	1.29	0.025	1.50	0.044	1.71	0.066	1.92	0.092	2.13	
1.09	0.008	1.30	0.026	1.51	0.045	1.72	0.068	1.93	0.093	2.14	
1.10	0.008	1.31	0.026	1.52	0.046	1.73	0.069	1.94	0.094	2.15	
1.11	0.009	1.32	0.027	1.53	0.047	1.74	0.070	1.95	0.095		
1.12	0.010	1.33	0.028	1.54	0.048	1.75	0.071	1.96	0.096		
1.13	0.011	1.34	0.029	1.55	0.049	1.76	0.072	1.97	0.098		
1.14	0.012	1.35	0.030	1.56	0.050	1.77	0.074	1.98	0.099		
1.15	0.013	1.36	0.031	1.57	0.051	1.78	0.075	1.99	0.100		
1.16	0.014	1.37	0.032	1.58	0.052	1.79	0.076	2.00	0.102		
1.17	0.014	1.38	0.033	1.59	0.053	1.80	0.077	2.01	0.103		
1.18	0.015	1.39	0.034	1.60	0.054	1.81	0.078	2.02	0.104		
1.19	0.016	1.40	0.035	1.61	0.055	1.82	0.079	2.03	0.106		
1.20	0.017	1.41	0.035	1.62	0.056	1.83	0.081	2.04	0.107		

DETECTOR UNIT

GALVANOMETER

GALVANOMETER CONTROL BOX

VARIAC

2 6
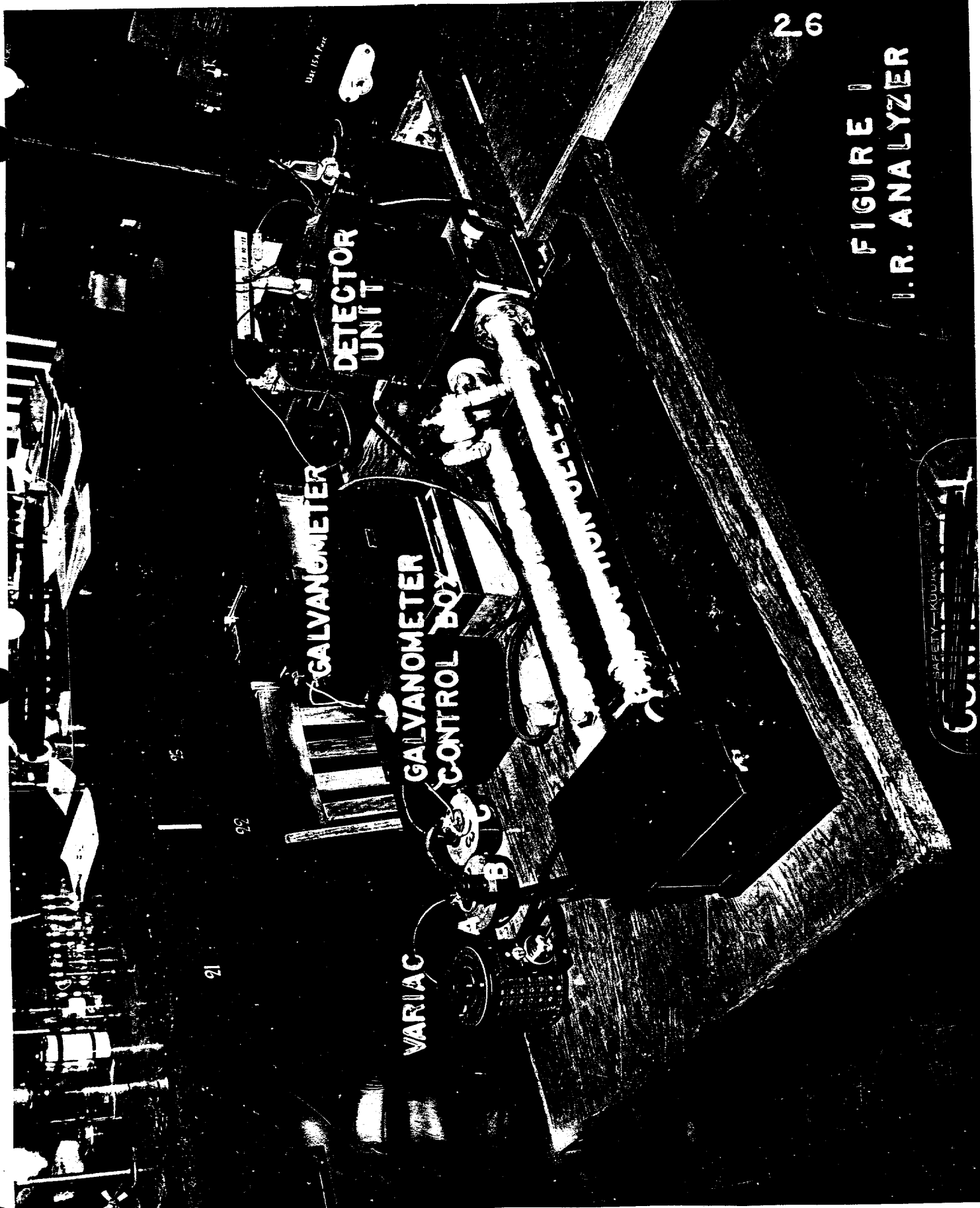
FIGURE I
I.R. ANALYZER

GALVANOMETER
CONTROL KNOB

SHUTTER
KNOB

MOTOR
SWITCH

2.6

FIGURE 2
I.R. SOURCE

CAPILLARY TUBE
CONTAINING
DEOBASE DROP

STOPCOCK BETWEEN
DETECTORS

LEVELING
SCREWS

Transfer System for Determination of FC in C-616

Refer to Figure 1.

1. Fill dewer flasks with tri-chlor-ethylene and crushed dry ice mixture.

2. Start the motor to the pump.

3. Attach absorption cell (1) and sample cylinder (5) to the transfer system.

4. Beginning from the pump, turn on valves (12) and (11) or (10) and (9), (depending upon which cold trap will be used); (8); (2); (3); (4); (1). Keep valves (6); (7); and (5) closed.

5. Evacuate the system until the manometer gives a differential reading of zero.

6. Close valves (1) and (2) and remove absorption cell for an evacuated reading in the gas analyzer.

7. After recording the evacuated reading, attach the absorption cell to the transfer system and open valves (2) and (1).

8. After the system has been evacuated, close valve (4) and adjust the manometer, by means of the stopcock, to the pressure desired. For FC analysis, the pressure should be 8 cm of Hg.

9. Turn on the switch to the standard RCA electron ray tube.

10. Close valve (8) and open valve (5) slowly.

11. By observing the electron ray tube, keep valve (5) open until the light begins blinking. When this occurs, close valve (5) immediately. Then close valve (1) and open valve (8). When the system is completely evacuated, close valve (8) and valve (2) and remove the absorption cell for a deflection reading of the sample in the gas analyzer.

NOTE: By manipulating valves (5) and (8) and watching the electron ray tube, the pressure in the absorption cell can be controlled within 8 cm of Hg $\neq$ 2 cm.

PRECAUTIONS:

1. Keep valve (4) closed at all times except when running an evacuated reading for the absorption cell.

2. Keep the transfer system free of moisture. This can be done by flaming the entire transfer system while evacuating it or keeping the system filled with dry nitrogen when removing the absorption cell, sample cylinders, or changing cold traps.

3. Always keep the valves closed on the cold traps when not in use. Be sure that the dewar flasks are filled with trichlorethylene dry ice mixture before using them.

FIGURE I
TRANSFER SYSTEM

2.6B
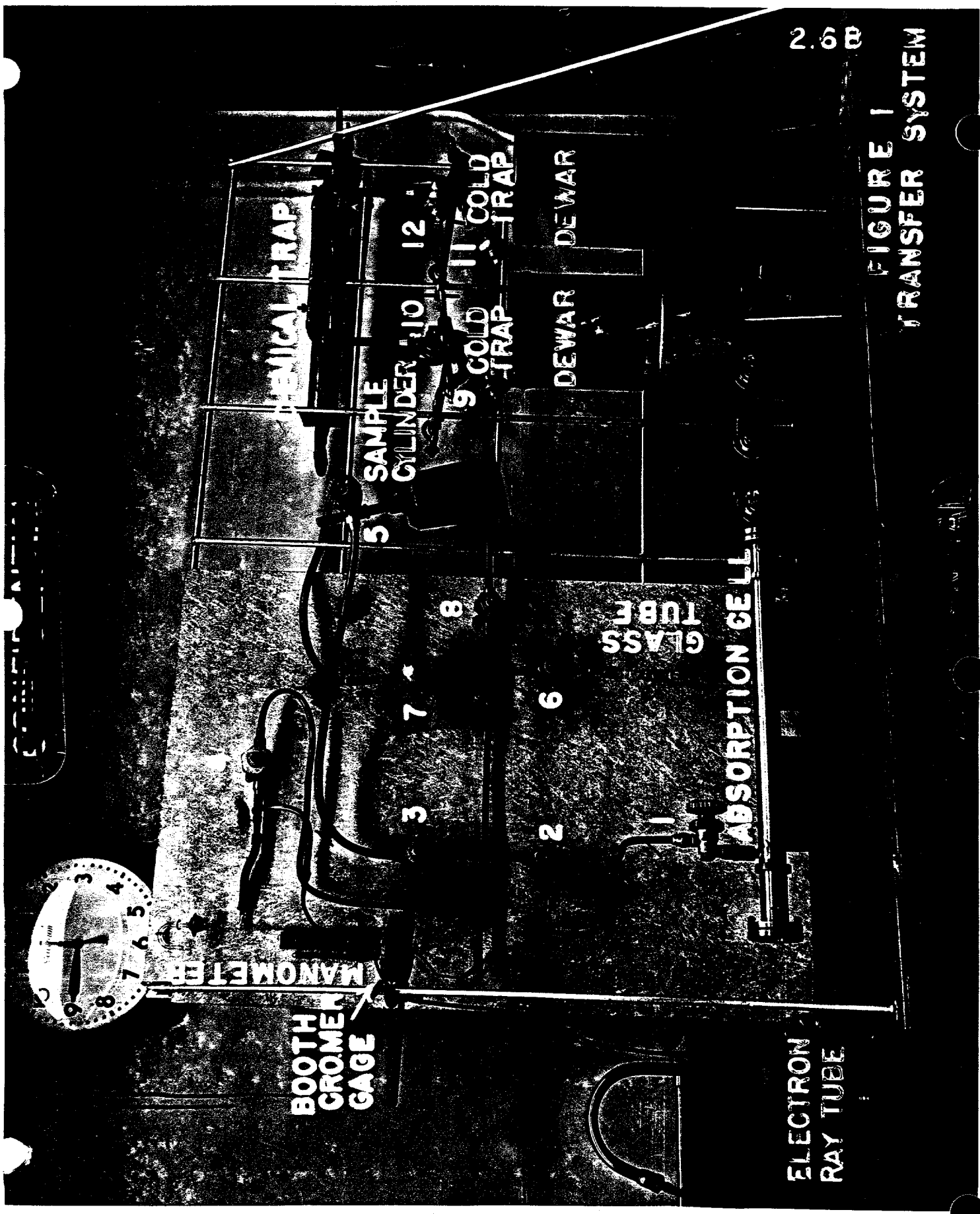
GENERAL INFORMATION

Sampling Section

I. Functions

This section is set up to handle a chemical known under the code name of C-616. The operations carried on by this section are:

A. Obtaining samples of C-616 in special containers for freezing point determinations and other control analyses by other groups.

B. Determining the purity of C-616, by determination of the freezing point.

C. Handling the transfer, removal, or collection of C-616, as a service to the rest of the laboratory and other groups throughout the plant.

II. Properties of C-616

There are three sub-classifications of C-616, known by code as, NBM, EBM, and DBM. For our purposes these three types are identical in physical and chemical properties.

The chief properties of C-616, relative to our work with it, are as follows:

A. Freezing point of the pure substance is 64.05° C.

B. Freezing point lowering is 0.067° C. per 0.01 weight per cent of HF, which is the most common impurity in C-616.

C. Both the solid and liquid have an appreciable vapor pressure. The vapor is a colorless heavy gas.

-2-

Temperature Deg. F.	Vapor Pressure – Lbs./sq. in. absolute
80	3
133	15
147 (M.P.)	22
212	60
220	70

Critical temperature - 232° C.
Critical pressure   - 50 atmospheres

D. Specific gravity of solid = 4.68

Specific gravity of liquid = 3.67

E. C-616 is a highly corrosive substance.   There are few materials inert to it.

1. It will react with water to form HF and a yellow, water soluble, non-volatile solid.

2. It is not a stable compound and is easily reduced. Reduction of C-616 results in a green, water-insoluble, non-volatile solid.

3. It will react with oils, greases, rubber, and any organic materials, with the exception of certain saturated fluorocarbons.

4. It will corrode most metals.

5. It and its products of hydrolysis are highly poisonous.

6. It will react with hydrogen and oxygen but is inert to nitrogen.

III. General Principles Regarding the Transfer and Sampling of C-616

The transfer of C-616 from one container to another may be effected by gravity flow in the liquid phase or pressure difference in the vapor phase.

The latter is the method customarily employed by this section. In very general terms, it consists of increasing the vapor pressure of the contents of the container from which material is to be removed, by raising its temperature, and decreasing the vapor pressure of the contents of the container which is to be filled, by lowering its temperature. With proper plumbing connecting the two, the flow of C-616 from the hot container to the cold container will then ensue. However, because of the reactive and poisonous nature of C-616, its transfer entails more than just that. The following rules govern the construction and use of any system carrying C-616:

A. Vacuum system: Any system or part of a system through which C-616 will flow, must be completely evacuated before introduction of C-616.

B. Dry and Outgassed System: Any newly constructed system must be completely dried and "outgassed" (removal of absorbed gases) before use, by heating tubing and empty containers and traps, while pumping on them.

C. Leak Tight System: Any system through which C-616 will flow must be leak tight, so that there is no flow of air from the atmosphere into the system while it is in operation. If air does leak into the lines, it will slow or stop the transfer. Also, the moisture in the air leaking in will hydrolyze the C-616, depositing the non-volatile solid product, which ultimately will plug up the tubing. For this reason a system must be leak-tested before each use in the following manner:

-4-

1. Evacuate the system to a vacuum of 30 in. of Hg. (If such a vacuum cannot be obtained, that is already an indication of the existence of a leak in the system).

2. Shut off the part of the system to be tested from the pump by closing the appropriate valve.

3. If there is no increase in pressure in the system within fifteen minutes, it may be considered leak tight.[*]

D. Traps

1. Cold traps: C-616 will react with the standard oil used in a vacuum pump, resulting in the formation of a sludge, which ultimately causes the failure of the pump. Also, C-616 is an expensive chemical and it is desired that its loss be kept to a minimum. Therefore, it is essential that no C-616 be allowed to pass through the vacuum pump. This is effected by having a cooled container or trap in which the C-616 is condensed, before the gases reach the pump. A section of a typical trap immersed in a cold bath is shown in Figure 1.

2. Chemical Trap: The simple cold trap, cooled in a trichlorethylene dry-ice bath is not one hundred per cent efficient in condensing C-616. In addition, HF, which is the most common impurity in C-616 and just as damaging to pumps as C-616, will get by the cold trap in greater part. It is

[*] See section VII for methods of locating leaks.

gradually along the tubing, always following the vapor ring that will form on the tubing just ahead of the flame. It is unsafe to heat the lines so that they become uncomfortable to the touch.

9. Close valves 3 and 2.

10. Wait for about ten minutes.

11. If system is leak tight, open valves 3 and 2.

12. Close valves 10, 11, 12, 13, 14, and 15.

heated by the torch. If the operator, for example, flames the U-tube first and there is some material plugging the line between the U and cold trap, a pressure will be built up.

9. The system is now being leak tested. If valve 3 is gas tight, then it is not necessary to close valve 2.

10. If after a ten minute wait the gauge still shows a vacuum of about 30 inches Hg,.proceed with the sampling. However, if the gauge has dropped during the ten minutes, locate and remedy the leak before continuing. For further procedures in leak testing, see Section C, below.

11. The system is opened to the pump and thoroughly evacuated.

12. The Hoke tube valves are closed at this time to prevent any non-condensibles present in the Harshaw from collecting in the tubes.

E.   Removal of Hydrofluoric Acid in Sampling: The most common impurity of C-616, as already mentioned, is hydrofluoric acid. In sampling work, unless otherwise requested, it is required that the samples be as free as possible from HF. (The HF content is already known from freezing point determinations.) The fact that a dry-ice trichlorethylene bath is not cold enough to condense HF out of a vacuum system, but cold enough to take out the C-616 is utilized in obtaining samples as free from HF as possible.

The sampling systems are built with a U-tube section between the sample receiver and the container from which the sample is to be taken. The U-tube is cooled down by immersion in a dry-ice trichlorethylene bath, and as the C-616 flows out of the container to be sampled, it is condensed in the U-tube. The tube, however, is open to the vacuum pump, so that the HF is pumped off from the condensed C-616. When it is judged that a sufficiently large quantity of C-616 has been collected in the U-tube, the valve on the container is closed, and pumping is continued for several minutes. The length of time required for this depends upon the purity of the material being sampled. The pump is then shut off from the tube by closing the proper valve, and its contents transferred to sample tubes, by heating the U-tube and cooling the sample receiver in liquid nitrogen. The sampling procedures give the details of this operation, as applied in any particular system.

F.   Shutting down of a System:. Before shutting down a system or opening it to the atmosphere, (i.e. when containers or tubes are being changed or removed) the following rules must be observed:

1. The tubing must be completely pumped out of all C-616.
   With the valves on all containers, except traps, closed,
   the lines are evacuated while being heated*, until all
   C-616 present is removed. This is checked by shutting off
   the pump line to the system, and observing the gauge over
   a period of five minutes. If the pressure starts building
   up, the presence of C-616 in the lines is indicated. If
   the pressure remains unchanged at 30 in. of Hg vacuum, the
   tubing may be considered free of C-616.

2. All valves on traps must be closed before the system is
   opened.

3. On systems where a dry nitrogen line is provided the best
   procedure is to fill the lines with nitrogen at slightly
   more than atmospheric pressure, (about one p.s.i.g.) before
   opening system. This prevents wet air from entering tube
   while the system is open.

G. Warming of Valves and Tubing: To prevent condensation of C-616
in the tubing or narrow passages in the systems, such as in valves, and
some fittings, and to improve the conditions of transfer, it is best to
keep the lines and valves, including those on containers and traps,
heated. This is generally accomplished by use of calrod or insulated
nichrome wire, or by use of infra-red lamps. The power input into the
heating elements must be controlled, so that the system never gets
warmer than 60-65° C.

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* Note Section VIII on safety precautions, in regard to heating tubing

IV. Equipment and Materials

A. Metals

C-616 will corrode most metals. The reaction of C-616 with some metals and alloys, such as nickel, monel, copper and brass, however, deposits an inert impermeable coating of the metal fluoride on the metal surface, sealing it off from further attack by C-616. Thus, on any system, or part of a system, which is to carry C-616, only nickel, monel, copper, or brass are to be used. The metal fluoride protective coat is hygroscopic; therefore wet air should be excluded from the system, even when it is not in actual operation. This is the reason for the policy of filling a system with dry nitrogen before opening it to the atmosphere.

B. Pumps

This section makes use of two makes of vacuum pumps:

1. The Welch pump: This is an oil-sealed positive displacement rotary pump, manufactured by the M. M. Welch Co. It comes in two small sizes, neither of which are suitable for large capacity systems.

    The level of the oil in the Duo-Seal pump must be maintained at the height marked on a small glass window on the side of the oil chamber. The Welch Co. sells the oil to be used in these pumps, but, if Duo-Seal oil is unobtainable, S.A.E. #30 oil may be used. Where a pump is in daily use, the oil should be drained out of the chamber and replaced with fresh oil at least every three

weeks. If the drained oil is particularly dirty and discolored, it is best to wash out the chamber with pump flush-oil before refilling.

If sufficiently large quantities of C-616 and HF pass through the pump, the result is an accumulation of sediment in the pump oil. In time this causes the resistance of the pump parts to motion to become so great that the motor is no longer able to operate the pump. A pump is said to "freeze" when this occurs. It can easily be ascertained as to whether the failure of a pump is due to freezing or to motor trouble, by trying to turn the pump wheel by hand, with the power shut off. If it can not be rotated, the pump is frozen.

2. The Kinney Pump: This is a vacuum pump of much larger capacity than the Duo-Seal pumps, and is used on large transfer systems. It has a large oil chamber or reservoir with an oil circulation system and a water cooling system. Because of this a definite procedure has to be followed in starting up or shutting down a Kinney pump. When the system is ready to be put into operation, the Kinney Pump is to be started up in the following manner:

(a) To Start up Pump: (1) Open valve wide on water line. Check for vigorous flow of water by observing flow from outlet pipe in sink. (2) Switch pump on (it takes 220 volts to operate the Kinney pump, so the pump is connected to the power line with a special switch box). (3) After

waiting about a minute, open the three oil systems valves.

(b) To Shut Down Pump: (1) Shut off oil valves. (2) Immediately shut off power. (3) Shut off water flow.

3. General Notes on the Use of Pumps

(a) Whenever a pump is shut off with its intake side remaining under vacuum, there is a tendency for oil to be sucked into the system because of the higher pressure on the exhaust side. This is obviously undesirable; so systems are constructed in such a way that air may be introduced into the intake line of the pump, after it is shut off, without the air getting into the traps or the rest of the system.

(b) Changes of oil and drive belts on Duo-Seal pumps may be made by this section. However, all other repairs to vacuum pumps, including change of oil or belt on Kinney pump, are the responsibility of the Vacuum Pump Shop.

C. Vacuum Pressure

1. Gauges

The pressure measuring instrument generally used by this section is a Bourden type gauge, with a range from 30 in. of Hg vacuum to 15 pounds per square inch above atmospheric pressure (p.s.i.g.). For use with C-616 the gauge must have a bronze tube.

Mercury manometers, unless used in conjunction with special pressure transmitters, are not suitable for use with C-616, since mercury is not inert to C-616.

D. Valves - Notes on Use and Installation

   1. Kerotest

      (a) This valve is received from the manufacturer with a fabric seat, which is highly reactive to C-616. A copper seat on a monel stem, or a seat of D-29 impregnated with 40 per cent Cu, must be installed in place of the fabric seat before this new valve is put into use.

      (b) The valve comes with either thread or solder connections for installation into a system. If the valve is to be soldered into place, the bonnet, diaphragms, bushing, spring, stem and copper gasket must be removed from the cell body before the soldering is done, otherwise damage to valve may result.

      (c) The valve should be installed so that the high pressure side is against the seat. Installation of the valve should always be made accordingly, so that the high pressure will not be on the diaphragm.

   2. Crane and Hoke Valves

     These valves are soldered in assembly so that the seals are not removable; therefore, when any soldering is done on these valves, they must be cooled by immersion in water or by wrapping in wet asbestos.

E. Gaskets

The ordinary type of gasket made of rubber or fabric will be corroded by C-616. Either an annealed copper gasket or one made of a specially designed plastic called D-29 which is inert to C-616, must be used on C-616 systems.

F. Containers

   1. Harshaw cell:

     This container was specially designed to hold the sample on which freezing point determinations are to be made. Its important features are shown in Figure 3.

   2. Hoke Sample Tube

     This container is designed to hold a small amount of sample for quality assay. A drawing is shown in Figure 4. Maximum safe load is 4-5 grams.

   3. B-Cylinders

     These cylinders stand about two feet high and are about 7" in diameter. They are used by this section as storage containers for C-616 emptied from Harshaw cells, traps, and other small cells. They are fitted with Chlorine Institute valves. The capacity of a B-cylinder is about 50 lbs.

   4. Other types of cylinders are occasionally handled, and the safety load limits of these must be known before filling.

G. Dewars

   1. Glass or thermos bottle type

   2. Large metal dewars

These are used to hold the coolant for B-cylinders or large traps. They have thin inner walls and a heavier outer jacket, with a valve outlet to the air space in the jacket. The jackets are evacuated to provide thermal insulation. The containers used in these dewars must not be allowed to rest on the bottoms, which are very thin. Re-evacuation of the jackets may be necessary from time to time.

V. Sequence of Operations

A. If the C-616 lot is received in any container other than a Harshaw cell, the first step is to obtain a 3-5 pound sample in a Harshaw cell, unless it is a special case where no freezing point determination is needed.

B. Freezing Point Determinations: This must be done before sampling. It can be readily seen that a vapor phase sampling may be considered as a distillation, and as such would result in a change in composition of the contents of the cell that is sampled.

C. Assay Sampling: This includes sampling for quality assay and chemical assay.

D. F..C. Analysis: Sampling for this analysis is done by a section in Room 17 and may be done prior to assay sampling, if necessary.

E. Emptying of Harshaw Cells: After completion of C.A. analysis by analytical services group, the contents of the Harshaw cell are emptied into a B-cylinder.

VI. Separation of Grades of C-616

The three general grade of C-616, as previously mentioned, are DBM, NBM, and EW; these in turn are further subdivided, each sub-division representing some particular isotopic ratio.

In the work of this sampling section it is necessary to keep all these grades, and subdivisions of grades, of material separate. This is done by using different traps and receivers for different grades of C-616, always using the same trap and receivers for the same grade.

Hydrolyzed C-616 must also be separated according to grade of material in solution.

If a trap is to be used for a grade different from the one for which it has been used, it must be thoroughly out-gassed, washed, dried, and then reconditioned with C-216 in order to restore the protective metal fluoride coat to the inner surface of the trap.

VII. Leak Testing and Location of Leaks

A. There are several methods for locating leaks in gas systems. The methods commonly employed by this section are the only ones discussed below:

1. Change in Leak Rate Method

    After a leak rate has been taken on the system, the suspected joint or fitting is covered with Apiezon-Q (a black clay-like material) making an air-tight seal over it. The system is then evacuated, and a leak rate again taken.

    If there is no leak this time, it is obvious that the given

joint was the souce of leak. If the system still leaks, but at an appreciably slower rate, then the given joint was only one of two or more leaks. Suspected sources of leaks are thus sealed, one at a time, with Apiezon-Q, and leak rates checked, until the actual source or sources of leaks are found as indicated by a change in the leak rate.

Apiezon-Q is not to be used to make a leak-tight system. It has a low melting point and is not inert to C-616. After a leak has been located the Apiezon-Q should be removed and the leak repaired.

2. Soap Bubble Method

The part of system suspected is filled with dry nitrogen at about 15 p.s.i.g. and the pressure is maintained by keeping a constant inflow of gas from the nitrogen cylinder. A bit of soap solution is then brushed on possible leak sources. The formation of soap bubbles at any point, indicates a flow of gas from the system, and thus the source of the leak.

If the leak is quite large, brushing with soap solution may be unnecessary, for the gas will probably leak out with an audible hiss.

B. Certain types of fittings on parts of systems are more likely to leak than others. The following is a list of the most common sources of leak:

1. Bad flare connections

2. Bad gaskets in adapters and couplings

3. Loose bonnets on valves

4. Bad solder joints

5. Defective or collapsed tubing

C. Leaky Valve Seat

The aforementioned techniques of leak testing will not re-
veal a leak across a valve seat. To determine whether a valve
in a system seats tightly, it is necessary to have a sizeable
pressure difference (at least 15 p.s.i. is best) between one
side of the closed valve and the other; if the pressure difference
is maintained the seat is tight.

.D. Apparent Leaks

It may occur that a system appears to be leaking and yet no
leak can be found. Often in such an event there is no actual
leak; one of the containers on the system may be leaking across
the valve seat, or condensed C-616 in the lines may be vaporizing.
The vapor pressure of C-616 at room temperature is approximately
25 in. of Hg vacuum. Thus, if the pressure builds up from 30"
of Hg vacuum to about 25" of Hg vacuum and stops there, it is a
good indication that C-616 is present in the lines or is passing
through a leaky valve on a cylinder.

Note that a good indication as to what to look for in leak
locating, is the point at which the pressure comes to equilibrium.
For example:

1. If the pressure in the system returns to zero (atmospheric
   pressure) then it is a leak from the atmosphere.

2. If the pressure comes to rest at approximately the vapor pressure of C-616 for that temperature, it is a leak through a valve on a container, or material in the lines.

3. If equilibrium is reached at a pressure other than that listed in the preceding two, it is a leak through a closed valve, from part of the system which is at a different pressure from that part which is under test, e.g. leaky valve on dry nitrogen line.

VIII. General Precautions and Safety Hazards

It is not the intention here to consider or review the general safety rules that are in force for the plant and laboratory. It is assumed that the operator has a general knowledge of the hazards present in any laboratory, and has been informed of the laboratory rules. The hazards and safety measures discussed here apply specifically to the type of operations carried out by this sampling group.

A. The vapor pressure of C-616 increases very rapidly with increase of temperature above its melting point. If a container of C-616 of the type or types generally used is heated much above 100° C., there is danger that the resultant pressure may exceed the load that the container can withstand, resulting in its bursting with explosive force. For this reason, when a container of C-616 is to be heated, it should be done either in a hot water bath, or a thermostatted oven set at not over 100° C. Also, when it is necessary to flame tubing that contains, or is thought to contain C-616, the

policy is not to heat the tubing hotter than the hand can stand.

B. C-616 expands on liquefaction as indicated by the data on specific gravities. Since cylinders filled with C-616 are usually heated above the melting point in the process of transfer, it is obvious that no cylinder should be filled, by vapor phase transfer, with so much C-616, that when liquefied the volume would be greater than that of the cylinder. Thus, the rule is that no container should be filled with solid C-616 to more than three-quarters of its total volume capacity. The maximum safety loads designated for containers discussed in the preceding sections, reflect this rule.

C. C-616 may condense, during transfer in a narrow passage in a valve, fitting, or section of tubing, and form a solid impassable plug. The most convenient and best means of removing the plug is to revaporize the C-616 by cautiously flaming the site of the plug, while pumping on it. If the plug is extensive, it is obvious that the best procedure is to start flaming at the pump side of plug and slowly progress to the opposite end.

It should be noted that this applies to a plug of solid C-616 and not one of hydrolyzed material, resulting from a leak. A plug of hydrolyzed C-616 is non-volatile and cannot be removed by flaming and pumping.

D. C-616 is a colorless gas. However, when it comes in contact with the atmosphere, hydrolysis takes place, so that finely divided products of hydrolysis are observed as white fumes. These products

of hydrolysis are equally as corrosive to organic tissues as C-616, causing respiratory irritation and severe skin burns on contact. Therefore, it is extremely important that great care be exercised in the operation of a C-616 system, so that no C-616 is allowed to leak out of the system or containers.

When a large leak or break in a system occurs, there is not only danger to the operator but to everyone else in the room. The immediate supervisor must be _instantly_ informed, in such an event, so that he may immediately take the necessary steps to rectify the situation.

E. If trichlorethylene and dry ice are mixed rapidly in large quantities, violent ebbulition will result, with the _usual_ consequence that a good part of the mixture will overflow the dewar and spill out on the bench and surrounding equipment. Addition of trichlorethylene to dry ice and vice versa should be done slowly and cautiously.

F. Trichlorethylene is a cumulative poison, and may be fatal to an individual inhaling the vapors continually in concentrations over 200 parts per million. Therefore, care should be taken that when making up the cold baths, or when working with trichlorethylene for any other reason, that as little of the vapors as possible are inhaled.

G. Trichlorethylene on hot copper or nickel yields phosgene. Do not flame any copper or nickel tubing that is wet with trichlorethylene. A case in point is the flaming of the U-tube after it has been immersed in dry ice-trichlorethylene bath. The U-tube should be warmed with hot water rather than a torch.

H. Glass dewars because of the vacuum jacket break explosively. To prevent the glass from flying about when a dewar shatters, the exterior glass surface of all dewars should be bound with friction tape. No dewar should be put into use unless properly taped.

I. The breaking of radiant or infra-red lamps also results in flying glass. It is not feasible to tape these, so extra care must be used in handling them. A drop of water on such a lamp, or the slightest contact with a cold surface, will shatter the lamp when it is hot.

KEROTEST VALVES

EXIT STREAM OF GASES 3.1
TO PUMP
MINUS C-616

ENTERING STREAM
OF GASES
CARRYING C-616

INNER TUBE EXTENDING
APPROX. 3/4 LENGTH
OF THE TRAP

A   B

C-616 CRYSTALS

TRICHLORETHYLENE - DRY ICE SLUSH

A - TRAP
B - DEWAR

FIGURE I
DRY ICE TRAP

COPPER GAUZE SCREEN
TO RETAIN FILLER

FROM
COLD
TRAP

A   B   C
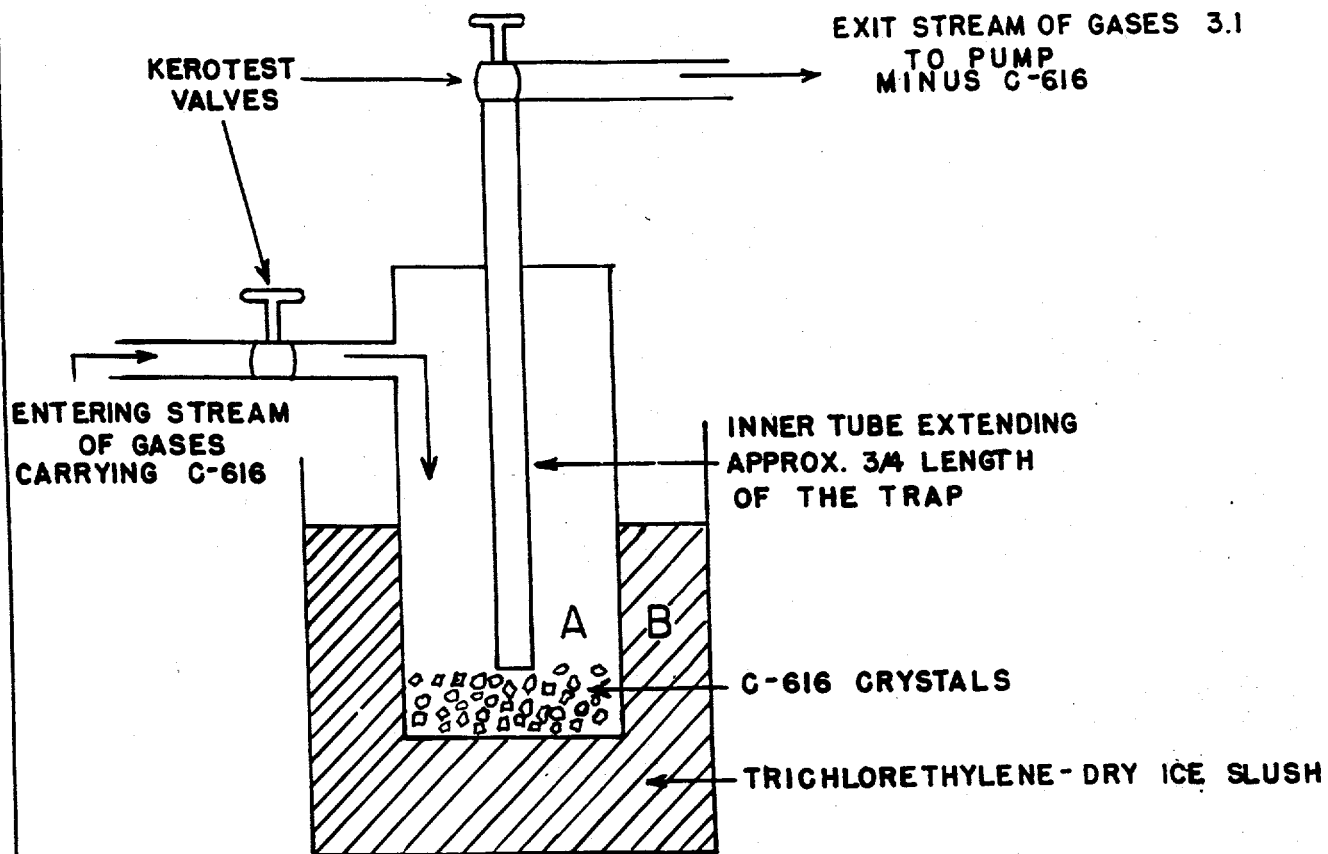
TO
VACUUM
PUMP
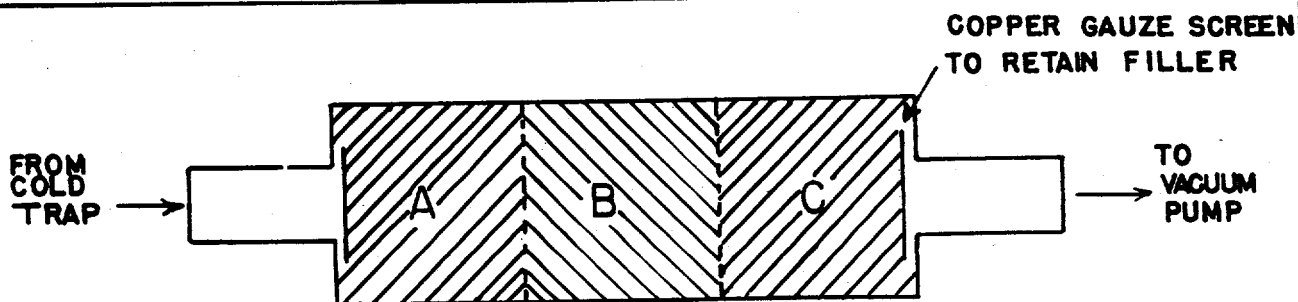
A - SODA - LIME - GRANULAR

B - ACTIVATED CARBON - PELLETS

C - DRIERITE - GRANULAR

FIGURE 2

TYPICAL CHEMICAL TRAP

BRASS OR COPPER PIPE
2" LONG - THR. 1 END

SILVER SOLDER

KEROTEST
VALVE 7903

SILVER SOLDER

3/8" BRASS TEE

SILVER SOLDER

3/8" x 2" BRASS NIPPLE

LITHARGE VISTANEX

NICKEL CYLINDER
APP. CAPACITY-765 CC
1.69" WATER

COPPER TUBE -11" LONG APP.
.375 O.D.-.311 I.D.

7 5/8"

1/2"

3 5/8"

1/8" THICK COPPER PLUG
SILVER SOLDERED

MODIFIED FREEZING POINT CELL

SCALE 6"=1'-0"

FIGURE 3

FEMALE OF HOKE UNION

RIGHT ANGLE
HOKE VALVE

OVERALL HEIGHT - 8 1/2"
MAX. SAFE LOAD - 4-5 GRAMS

1/4" NICKEL TUBE
APPROX. 6" LONG
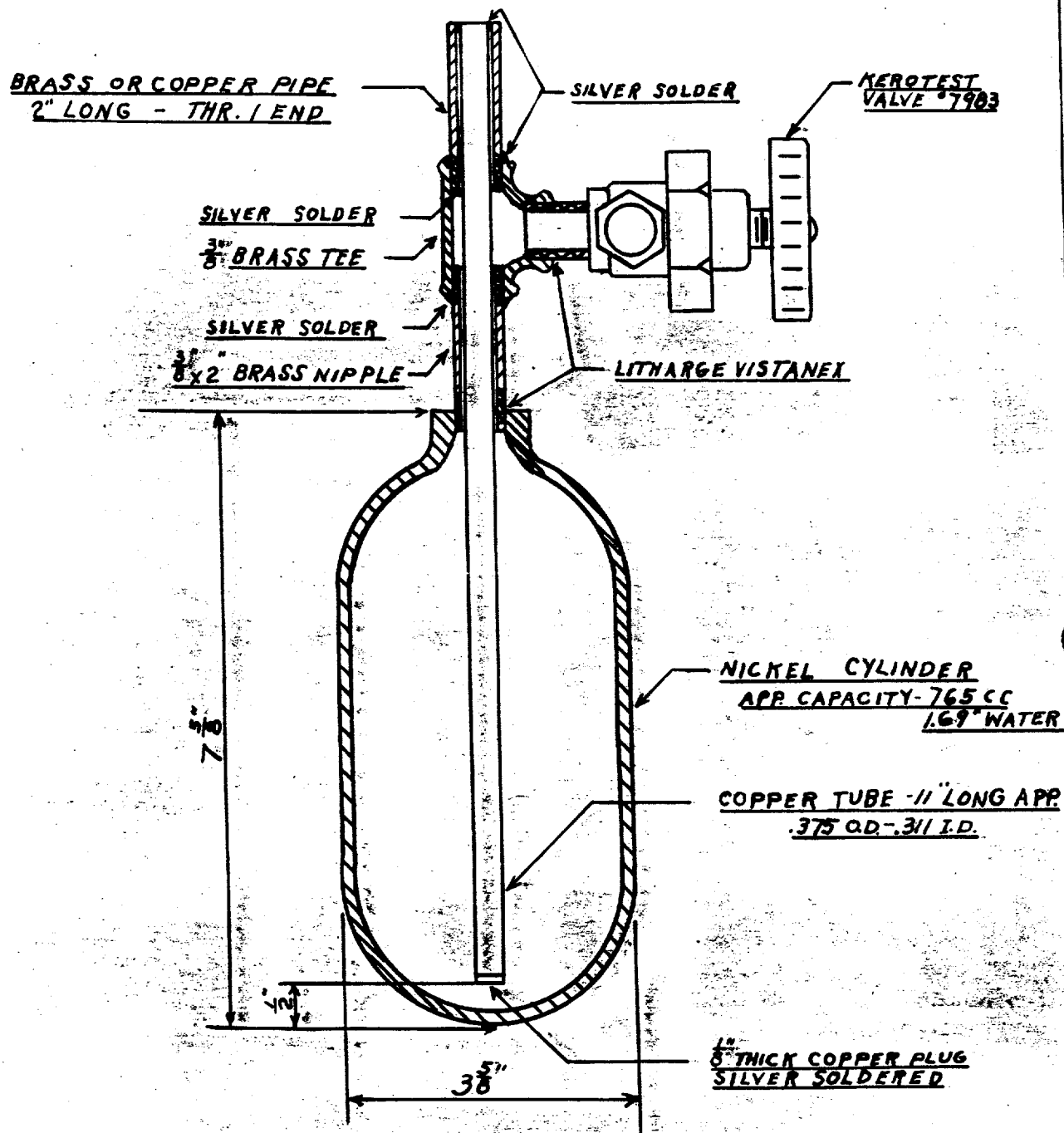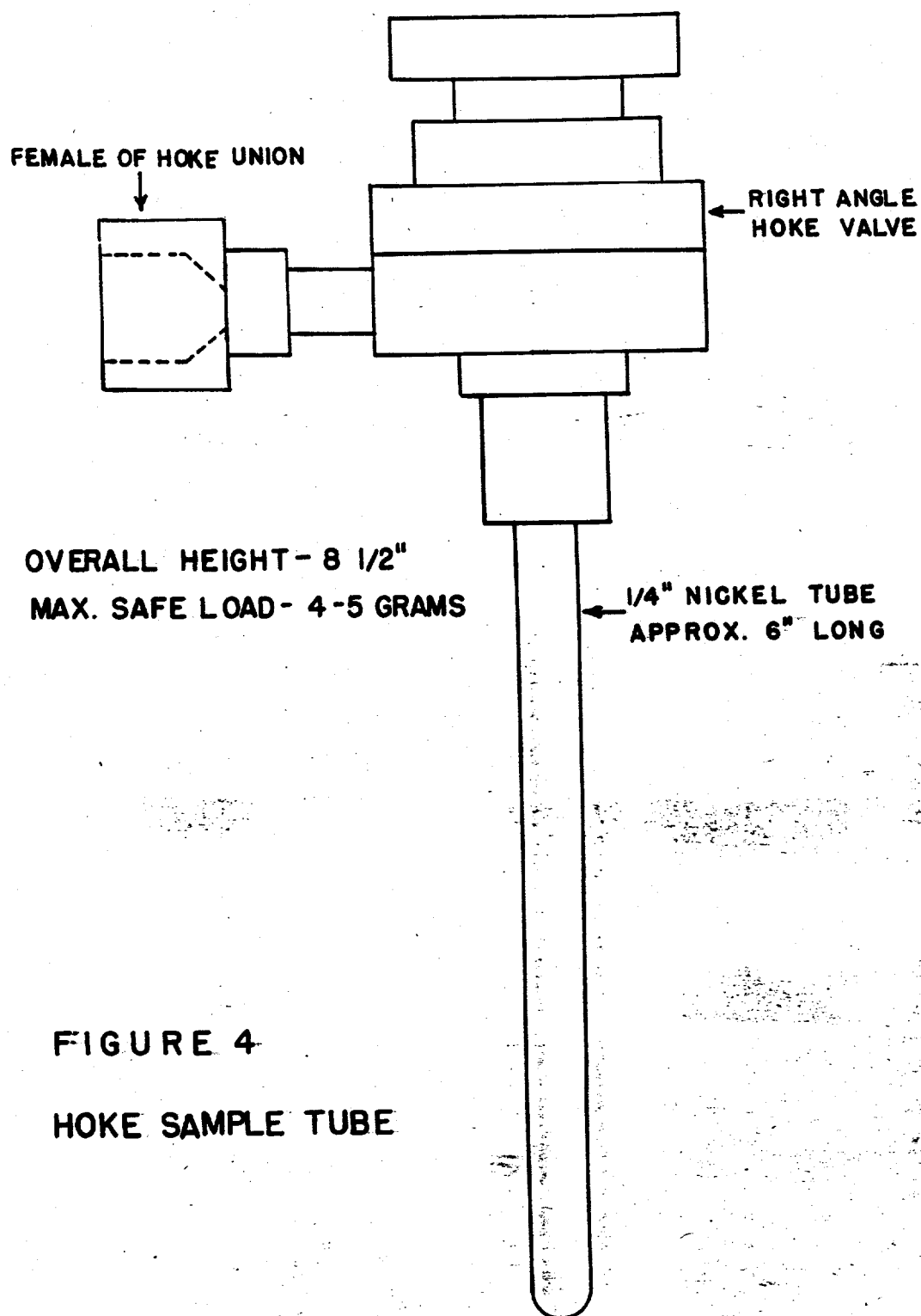
FIGURE 4

HOKE SAMPLE TUBE

MOBILE SAMPLING FOR LARGE STORAGE DRUMS OF C-616

Vapor Phase Transfer

Samples weighing from 2-1/2 to 4 pounds are needed from 4500 lb. chemical warfare storage drums of C-616, so that freezing points may be run on the material. To take these samples, a mobile sampling unit has been constructed on a truck, in order that sampling may be done in the storage lot.

A gasoline-driven generator supplies the power for the Welch vacuum pump and the bank of infra-red lamps for heating the storage drum. Care must be exercised to see that the voltage does not exceed 115 volts, which would burn out the pump motor. To accomplish this, there is a governor in the generator to regulate the speed, and a volt-meter to check the voltage periodically.

The entire vacuum system (See Figure I) is made of 5/8" copper tubing wound with nichrome resistance wire to heat the lines to $50-60^\circ$ C. The lines should never be allowed to become warmer than 60° C., for the vapor pressure of C-616 begins to rise at a rapid rate at that temperature. Control of the temperature of the resistance wire is maintained by use of a variac.

A. Preparation of System for Operation

1. Ice the cold trap in a bath of trichlorethylene and dry ice. Allow to stand for 10-15 minutes, to insure that all C-616 in the trap is completely frozen.

2. If the weather is cool, warm the oil in the pump by means of an infra-red lamp.

3. Attach adapter to large tank, and then connect the 1/2" union, as shown in the diagram. At other end of flexible tubing, connect Kerotest valve 1.

4. Set up the lamp bank for heating drum and valve. Start heating the system lines by connecting in the nichrome wire. Set the variac at 120 at the start, and as the lines begin to warm turn it down.

5. Attach empty Harshaw cell at point shown on diagram.

6. Evacuate system to 30" Hg vacuum, then close pump off from rest of system, by closing valve 7, and leak test. If after about 5 minutes there is no apparent movement in the gauge, it can be assumed that the system is tight.

7. Close Harshaw valve, and immerse about three quarters of the cell in liquid nitrogen (L-28) contained in a dewar.

B. Operations for Taking Sample

Operation	Reason for Operation
1. Open valve A and valve 1. Keep valve 2 closed.	1. By this means the initial pressure in the storage drum is obtained. This is usually from 10-26" vacuum pressure.
2. Close valve A; open valve 2 to pump.	2. This removes C-616 introduced into lines by initial pressure test. (About 5 minutes required).
3. Close valve 2; open Harshaw valve; open valve A.	3. Gas should now begin to condense in Harshaw cell.

4. Play gas-oxygen flame on valve and upper part of Harshaw cell.

4. This prevents condensation of C-616 in valve or near top of cell. WARNING: DO NOT HEAT CELL ANY WARMER THAN IS COMFORTABLE TO THE TOUCH. However, since the cell must be kept warm, it is necessary to repeat the flaming procedure at regular intervals.

5. Close valve 1.

5. This will give a rough estimate of the condensation rate. If the gauge drops from 25" vacuum to 30" vacuum in 5-10 seconds, the gas is condensing at a good rate. If, however, there is no drop in pressure, the non-condensibles in the C-616 have built up in the Harshaw cell to such an extent that they must be pumped off before further transfer can be made.

6. Open valve 2.

6. This allows non-condensibles to be pumped off, and usually requires about a minute. The frequency of this operation is dependent upon the amount of impurities in the C-616.

7. Close valve A; close valve on Harshaw cell; open valve 2.

7. This is carried out when the cell is full, or it is to be removed for any reason. This removes the C-616 from the lines.

8. Close valve 6; open valve 5. Repeat several times.

8. This operation purges the lines with G-74, further assuring that all C-616 is removed. WARNING: THIS STEP SHOULD ALWAYS BE TAKEN BEFORE CELL IS REMOVED FROM SYSTEM OR ANY PART OF SYSTEM OPENED TO AIR.

9. Pressure system to 5 p.s.i.g. with G-74 before opening to air.

9. This prevents any inleakage of moist air.

Always make sure valves 2, 5, 6, and 7 are closed before opening the system to the atmosphere. Immediately after shutting off the vacuum pump, the California valve, in the line between chemical trap and pump, should be opened. This is done to equalize pressure in the pump and prevent diffusion of oil from the pump into vacuum lines.

The length of time required to take a sample is difficult to estimate, due to the variations in impurities in the drums. However, on the average, two hours are necessary for a sample.
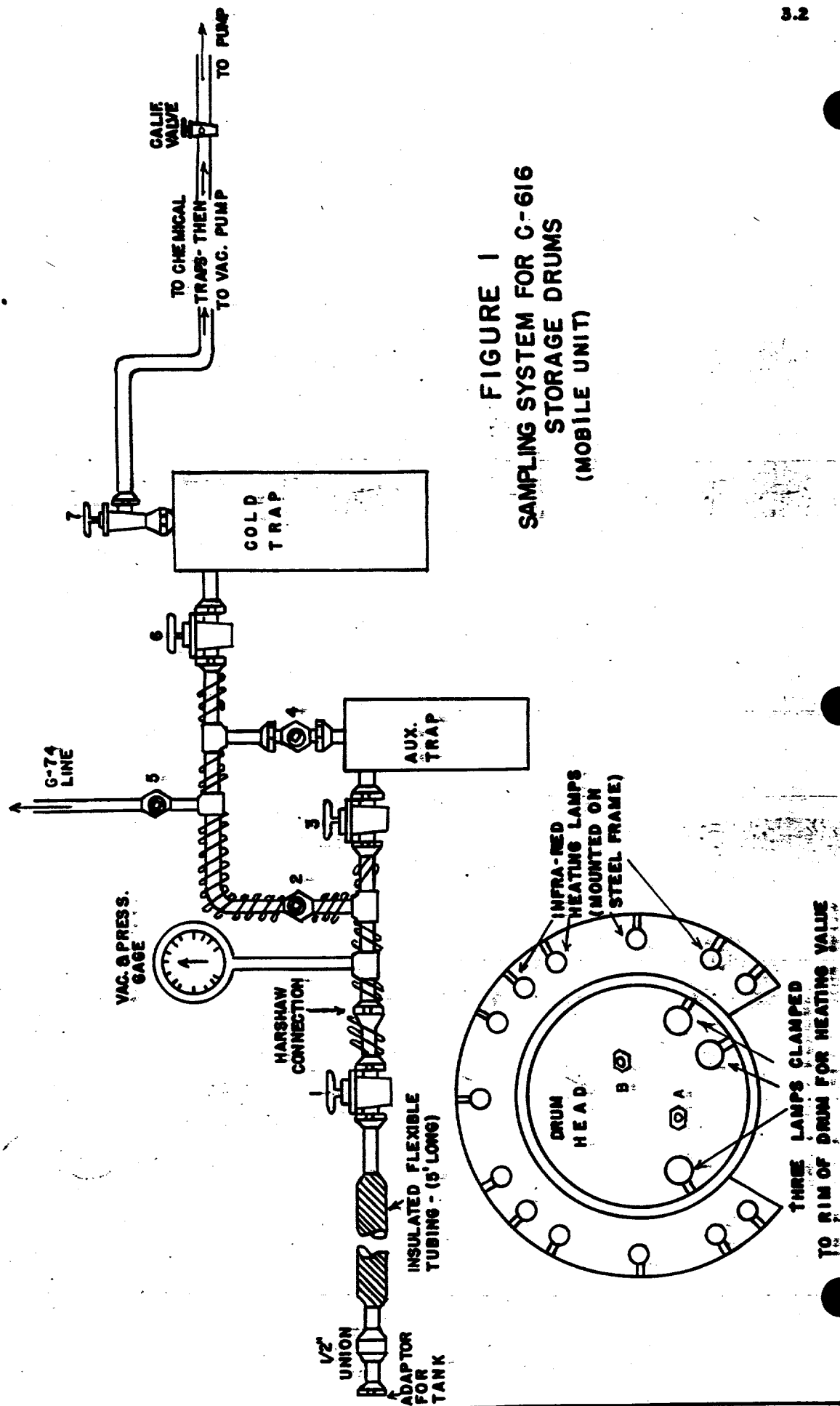
FIGURE 1

SAMPLING SYSTEM FOR C-616
STORAGE DRUMS
(MOBILE UNIT)

VAPOR PHASE SAMPLING SYSTEM FOR C-616

(Storage Drums)

The purpose of this transfer system is to obtain a small sample of C-616 from each storage drum. Approximately 2-1/2 to 4 pounds of material are needed from each drum in order to run a freezing point. The drums are C&CCC cylinders having a capacity of about 300 to 400 pounds.

The transfer is done in the vapor phase and is carried on through a vacuum system. A Kinney pump is used to produce the necessary vacuum throughout the system. (Knowledge of the operation of the Kinney pump is assumed).

I. Apparatus (See Figure 1)

The system consists of a Kinney pump to which is attached a trap with a capaity of approximately 40 lbs. of C-616. Valve 1 is a 1/2 inch SM Crane valve, 2 and 3 are 1 inch SM Crane valves. The gauge is an Ashcroft bronze tube duragauge. The tubing attached to the inlet arm of the trap is 5/8 inch copper tubing. The connection for the Harshaw cell is a 1/2 inch flare nut. The large sample drum is heated by a bank of three 250 watt infra-red bulbs in order to increase the vapor pressure of the C-616 and facilitate sampling.

II. Procedure

    A. Preparation of the System for Operation

        1. Close all valves.

2. Ice down the cold trap in a slush bath of dry ice and trichlorethylene. Allow this to stand for about ten to fifteen minutes to insure that all C-616 in the trap has solidified and will not be pulled into the pump when the system is evacuated.

3. Attach the storage drum to the system by means of an adapter, and attach the Harshaw cell at the point shown on the diagram.

4. Turn the lamps on the storage drum and heat it.

5. When the cold trap has cooled thoroughly, open it to the pump and leak test the entire system as follows: Open valves 1, 2, 3, and the valve on the Harshaw cell, and thoroughly evacuate the system. Close Crane valve 1 and allow the system to remain this way for about five minutes. If, after this time, there is no apparent movement in the vacuum gauge, the system can be assumed to be leak tight.

6. Close the valve on the Harshaw cell and cool cell by immersing 3/4 of it in a dewar of L-28.

B. Operation of the sampling system.

Operation	Reason for Operation
1. Close valve 1 and the Harshaw cell valve. Open valve "A" on the cylinder to be sampled.	1. This will indicate the intial pressure in the storage cell, thus assuring that there is some material in the drum, and also indicating frozen valves. (This pressure is usually 10 inches to 15 inches of mercury.)

2. Bleed down the pressure until it is approximately 25" vacuum by the following procedure: Open valves 1 and 2, allowing the C-616 to expand into the cold trap. Close valve 2, open 3 and pump the system out. Repeat this procedure until the desired pressure of 25" vacuum is obtained.

2. This will cause a large amount of the HF and non-condensibles to be pumped off and be caught in the cold trap. The length of time required for this is usually not more than three to four minutes, but is largely dependent on the purity of the material.

3. Close "A" and open valves 1, 2, and 3.

3. This will clean out the material in the lines before actually starting the transfer process.

4. Close valve 1, open Harshaw valve and also valve "A". Valves 2, and 3 remain open.

4. The C-616 vapor should now condense in the Harshaw cell which is cold in the L-28.

5. Play the gas-oxygen flame on the Harshaw valve, the upper part of Harshaw cell, and over the system lines.

5. This prevents the valve and upper portion of Harshaw cell from becoming too cold and thus becoming plugged with condensed C-616. There is also the same danger of plugging if the lines become too cold.

WARNING: NEVER HEAT THE CELL OR LINES TO A POINT WHERE THEY ARE NOT COMFORTABLE TO THE TOUCH. However, these parts should be kept quite warm at all times and, therefore, this heating operation has to be carried on at regular intervals.

6. Close valve A to check condensation rate.

6. By closing valve "A" and leaving valve 1 closed and the Harshaw valve open, a condensation rate may be roughly observed. If the vacuum gauge drops from 25" down to 30" vacuum in a short time (about five to ten seconds), the gas is condensing in the Harshaw cell at a good rate and only 20-30 minutes will be required to collect the desired sample. However, if there is no apparent drop in the gauge, the non-condensibles have built up to such an extent that they must be pumped out before further transfer can be made.

7. When non-condensibles have built up: Close A, open valves 1, 2, 3, and evacuate to sampling pressure (24-26" vacuum).

7. By this means the non-condensibles are pumped off; usually about one minute is required. The frequency of this operation is dependent upon the amount of impurities in the C-616.

8. Close valve 1, open A, and resume operations as in operation No. 4 above. The time will depend on the condensation rate.

8. Self-explanatory.

9. Close valve A, close Harshaw valve, and open valve 1. Allow the system to pump out for about five minutes.

9. This is done to pump out all the C-616 in the lines before removing the Harshaw or opening any part of the system to the air.

Always close valves 1, 2, and 3 before opening the system to the air. These Crane valves are tightened by means of a wrench whenever the system is to be shut down. This is to make certain that no C-616 vapor will escape into the lines or room when the trap warms to room temperature.

The length of time required to obtain the desired sample is difficult to estimate, but approximately thirty to forty minutes are usually sufficient to obtain a sample of 2-1/2 to 4 pounds. A great deal can be learned about the length of time needed to obtain a sample from observing the condensation rate as explained in Operation 6.

FIGURE I

SAMPLING SYSTEM FOR C-616
STORAGE DRUMS
(VAPOR PHASE TRANSFER)

300 LB. C&CCC STORAGE DRUM

SYLPHON TUBING

VAC. GAGE

HARSHAW CONNECTION

CRANE I

I" N I UNION

CRANE 2

COLD TRAP

CRANE 3

CALIB. VALVE

TO KINNEY PUMP
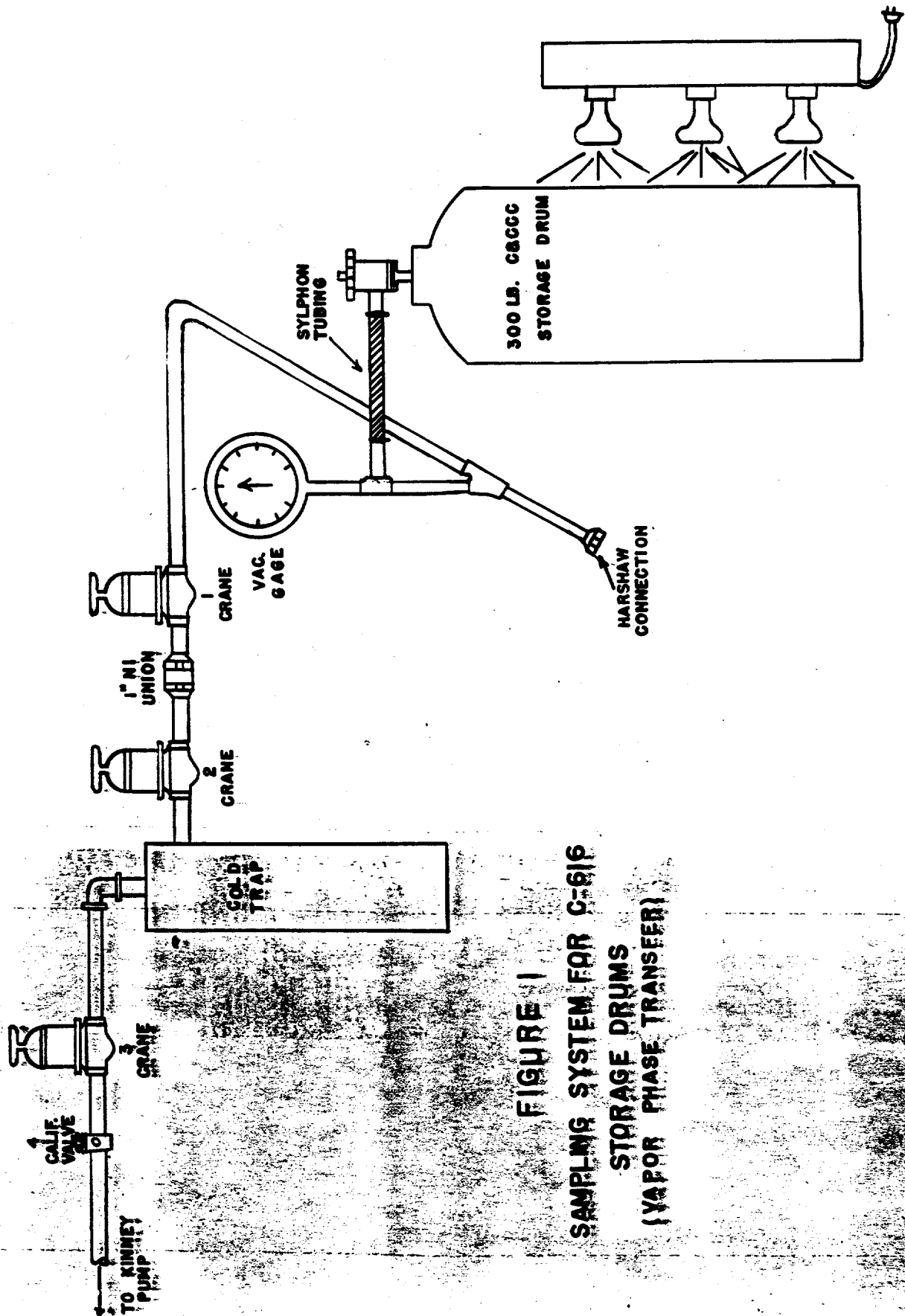
ASSAY SAMPLING

I. Purpose of Assay Sampling

The purpose of the Assay System (from now on referred to as the C.A. system) is to provide a way to transfer C-616 from Harshaw cells to thin-walled glass tubes from which the C-616 is later removed for chemical assay. This system is also used to transfer C-616 from Harshaw cells to Hoke tubes. This latter method is called Quality Assay Sampling whereas the glass tube method is called Chemical Assay Sampling. Since the method of transferring the sample to the Hoke tube is identical in procedure to that of the NBM sampling system, please refer to the NBM report and adapt its information for use with the C.A. system.

II. Description of the Construction and Use of the Glass Tubes

A. Building the tube

The building of the tube is a cooperative effort. The glass blower in Laboratory A makes the tube part A to B as shown on the diagram. The taper part of the tubes are supplied by the stock room in Laboratory D. The glass blower of Room 4 in Laboratory D is responsible for the fusing together of the taper and tube, and for making the constriction, the use of which will be described below.

Each taper is assigned a number which is etched on its neck by a diamond point electric pencil. This number is recorded in the C.A. sampling book in the section devoted to taper records. The tapers are used as many times as possible and each new tube attached to the taper is assigned the taper number and also the current tube number. For example, if the current tube was the fourth attached to taper number 121, the number etched on the tube would be 121-4.

After all the tubes have been marked the tubes are dried for about thirty minutes in a desiccator which is kept under vacuum conditions in an oven. After the tubes have been dried and cooled to room temperature, they are taken to Room 21 where they are weighed carefully to a tenth of a milligram. The tubes are then returned to this department ready for use.

Glass tubes are used as sample containers as it is necessary that the sample material be transferred from the glass tube to solution without coming in contact with air. This is effected by holding the sample bulb of the glass tube under water and pressing the thin glass breaking stirrup with a breaking tool. The sample released goes into immediate solution.

B. Sealing off of the Tube after Collecting the Sample

After the sample has been collected in the glass C.A. tube and the lower portion of the tube has been completely immersed in liquid nitrogen (L-28) the tube must then be sealed off at the constriction. The sole purpose of the constriction is to facilitate the task of sealing off the tube. To do this, gently play the oxy-gas torch around this constricted section of the tube, heating it all evenly. If one portion is heated too much, the vacuum in the tube will cause the thin-walled constricted area to collapse, allowing air to enter the tube and ruin the sample. During the early heating the tip of the flame should be used, but as soon as the constriction begins to show a slight reddish glow the flame should be moved closer to the tube so that the inner cone of the flame is almost touching the constriction.

It is necessary that the operator support the lower part of the tube during this operation. As soon as the glass is soft enough the operator should move the lower part of the tube slowly to the left and up. The flame should be squarely on the thin section during this operation and as the tube separates the operator should play the flame over both ends of the break, assuring a perfect seal.

The tubes are then allowed to stand in a hood, until they reach room temperature. It is possible that the tubes will explode as the sample gradually expands, due to the change in temperature. Resamples must be taken when a tube explodes.

Finally the tube and its taper are taken together to Room 21 for weighing, where a T analysis is run on the sample.

III. Preparing the System for Operation

A. Attach Harshaw of C-616 to "A" on diagram.

B. Freeze down the cold trap in a dewar containing a slushy mixture of trichlorethylene and dry ice. Let the trap stand for almost fifteen (15) minutes before it is evacuated. (For a discussion on the use of cold traps in systems handling C-616, please refer to the general report on Sampling Techniques).

C. Set the variac controlling the nichrome resistance wire at approximately 100 volts until the wire becomes quite hot to the touch. Then set the variac back to about 90. The actual setting should be governed by the temperature of the system.

D. Prepare a dewar of trichlorethylene, and dry ice slush - the use of which will be discussed later in this report. Also have a can of hot water ready and several small dewars along with a supply of L-28.

E. Attach 4 C.A. tubes to the system. Use Apiezon-L stopcock grease to form an air tight joint between the male and female tapers.

IV. Operation of the C.A. System (Refer to diagram of the System)

Operation	Need for Operation
1. Turn on vacuum pump (all other valves are closed).	1. The sampling is a vapor phase transfer run under vacuum conditions.
2. Open Valve 12.	2. The pump is now evacuating the chemical trap, which is the final barrier in the system, with the purpose of removing final traces of C-616 and preventing same from getting to the pump.
3. Open Valve 11.	3. This valve opens the line to Valve 10 on the cold trap.
4. Open Valve 10.	4. The pump is now evacuating the cold trap. The purpose of the cold trap is to collect and condense C-616 vapors. Much excess material leaves the Harshaw during sampling and this material must be collected at some point, thus the cold trap.

5. Open Valve 9.

5. This operation opens the pump to the system proper.

6. Open Valve 8 and then Valve 7.

6. The entire system up to the Harshaw cell is now open to the pump.

7. Open Valves 3, 4, 5, and 6.

7. The opening of these valves makes it possible to evacuate the C.A. tubes.

8. Close Valve 8.

8. It is now necessary to leak test the system.

(For leak testing procedure please see the NBM report. The gauge readings for the two systems are identical).

9. Close Valves 3, 4, 5, 6

9. Non-condensibles should be kept out of the C.A. tubes.

10. Open Harshaw cell Valve H and take an initial pressure reading. Bleed down the cell if necessary. Close Valve H.

10. The pressure should be about 25" of Hg vacuum. However, DBM material usually is contaminated with quite a bit of non-condensibles and it is necessary to alternately open valves H and 8 in order to bleed the pressure down to 25" of Hg vacuum.

11. Open Valve 8.

11. It is necessary to pump on the C-616 being collected for sampling in order to remove the non-condensibles.

12. Gradually chill down U-tube with slush mixture of tri-chlorethylene and dry ice con-tained in dewar. After lower 2" of U-tube have been cooled open Harshaw Valve H and continue raising the dewar until all of U is immersed in the cold mixture.

12. The C-616 from the Harshaw cell will concentrate in the U-tube in the form of a condensed solid material. This material will be then used as the sample material.

13. After about a total elapsed time of 45 seconds close Valve H.

13. Enough material should have been collected in the U-tube during that time.

14. After about three more minutes close Valve 8.

14. During that time practically all non-condensibles should have been pumped out of the system.

15. Immerse U-tube in container of hot water.

15. The actual sampling takes place as a vapor phase transfer. The hot water vaporizes the solid C-616 in the U-tube.

16. Secure small dewar of L-28 into position so that the lower half of the sample bulb is immersed in the L-28.

16. The vaporized C-616 should go to the bottom of the tube before it is condensed.

17. Open Valve 3.

17. The opening of this valve allows the C-616 to enter the tube.

18. After about 15 seconds, close Valve 3.

18. It takes about 15 seconds to collect a sample of solid C-616 in the range of 1.0 to 3.0 grams. As this phase of the operation all depends upon good estimation by the operator - experience is the only way that an effective technique can be developed. Throughout the collecting of the sample the upper part of the tube should be tapped if the C-616 begins to gather in the narrow capillary.

19. Raise dewar so that approximately 2 inches of the C.A. tube is immersed in the L-28

19. It is necessary to keep the sample well frozen down while the tube is separated by the flaming method.

20. Separate the lower part of the tube from the taper at the constriction.

20. The method has been described previously.

21. Record all pertinent data such as taper No., tube No., lot No., etc., in C. A. sampling book.

21. Self explanatory.

22. Repeat steps 16 through 21 for each C. A. tube.

22. Self explanatory.

23. The system is now ready to shut down. It should be in this state: Valve 1 open, Valves H, 2, 3, 4, 5, 6, and 8 closed.

23. Self explanatory.

24. Open Valve 8.

24. The excess C-616 can now be pumped out of the lines, U tube, and into the traps. Pump for several minutes, and gently heat the U tube.

25. Close Valve 8. Open Valve 7, and allow C-74 to fill the system to a gauge pressure of about $+$ 5 lbs.

25. This is the first step in purging the system.

26. Close Valve 7, open Valve 8 and pump out the system thoroughly. This filling with C-74 and pumping out should be done at least twice.

26. The residual C-616 in the system is swept out by this process.

27. Once more fill the system with G-74, but this time to a pressure of only 1 lb. gauge. Close Valve 1, remove Harshaw cell, and plug the flare nut on the end of the U tube.

27. This process will prevent the introduction of wet air into the system.

28. Close valve 9, 10, 11, and 12. Shut off pump.

28. It is necessary to follow this procedure in shutting down the system.

29. Open Valve C until pressure in the pump reaches atmospheric, then close it.

29. Oil will diffuse from the pump into the system unless this is done.

30. Turn off the variac.

30. The heating unit is now off.

FIGURE 1
DIAGRAM OF GLASS SAMPLING TUBE

Standard ¹⁰/₃₀ Female Taper

Taper Number

Joint-A

Constriction

Tube Number

Indentation

Sample Bulb

Approx. 8"

121

121-4
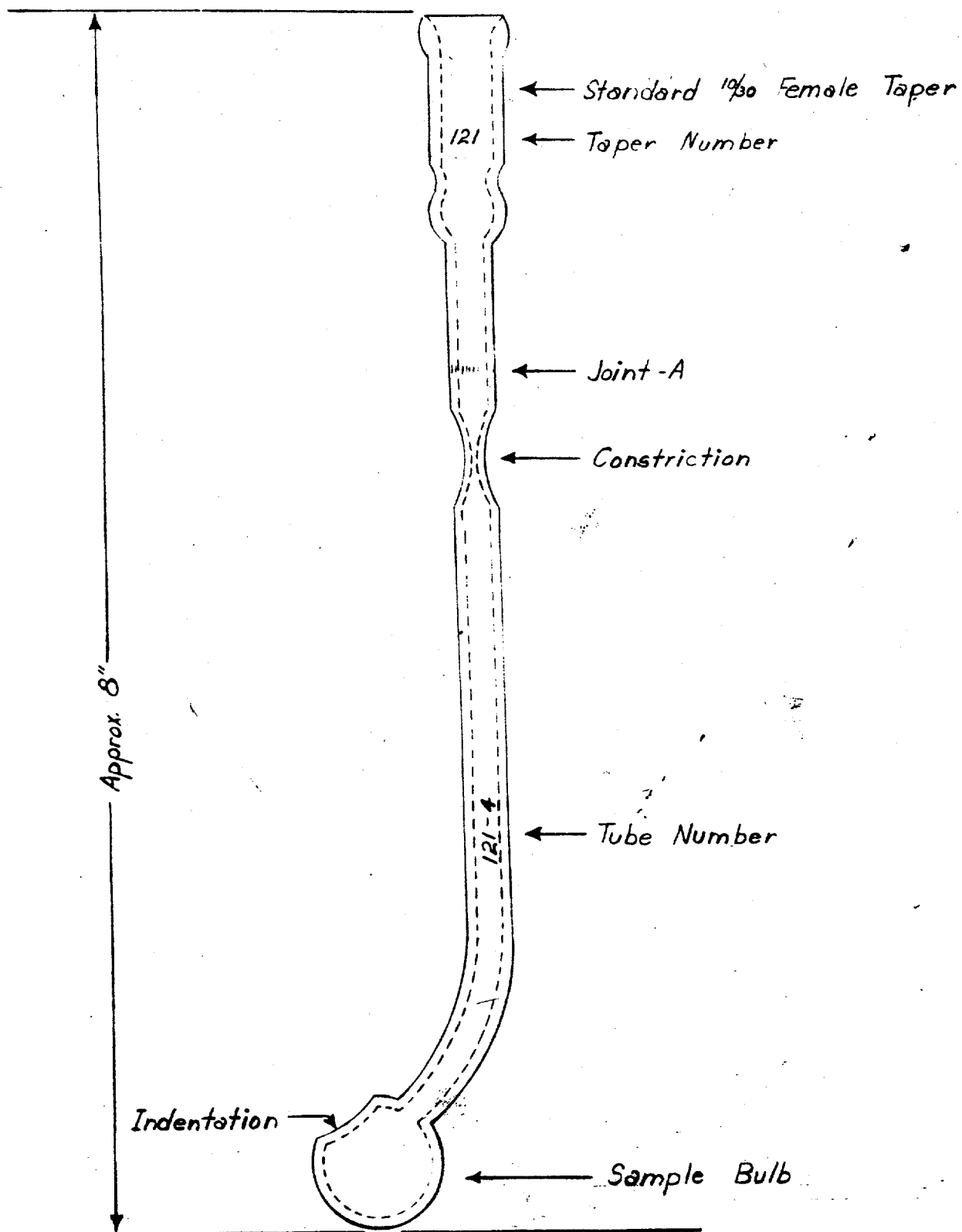
FIGURE 2

CHEMICAL ASSAY SAMPLING SYSTEM
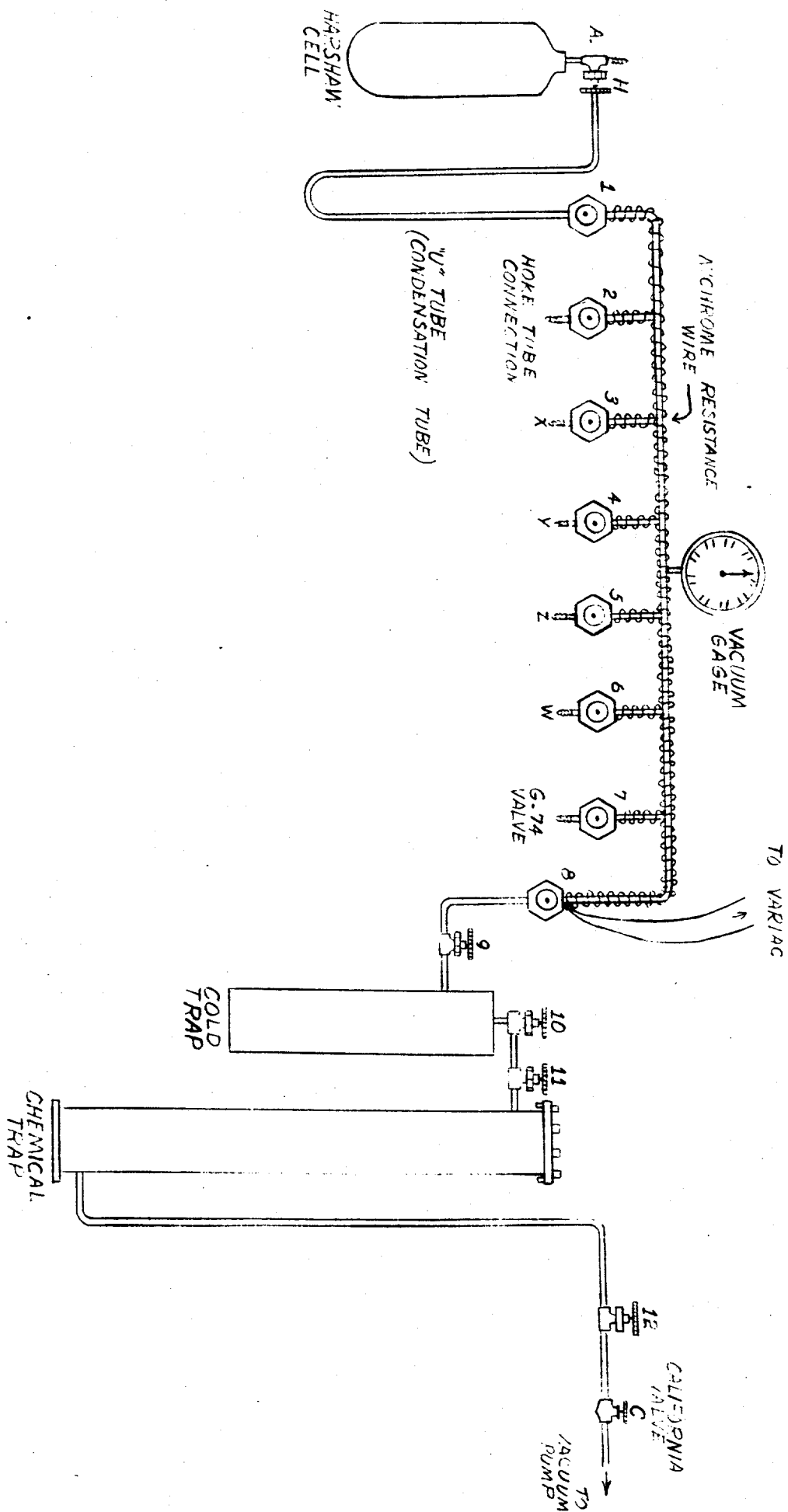
OPERATION OF THE NBM SYSTEM

I. Purpose

A. To transfer samples of NBM C-616 from Harshaw cells to sample containers known as Hoke Tubes for isotopic analyses.

B. To transfer large quantities of NBM C-616 from Harshaw cells to various type containers for field use.

C. To empty NBM C-616 from various containers such as traps, Harshaw cells or many other different types of NBM containers.

II. Hoke Tube Sampling

A. Preparation

1. In order to insure condensation of NBM C-616 in the cold trap, (see Figure 1) place a large dewar so that it surrounds the trap and leaves about 1 inch of the trap walls above the lip of the dewar.

2. Add trichlorethylene and dry ice to the dewar until all but about 3 inches of the trap are immersed in the mixture. The final consistency of the trichlorethylene and dry ice mixture should be that of a loose slush. This cold mixture will freeze the C-616 already in the cold trap and also freeze the vaporized C-616 that is drawn into the trap during operation of the system.

3. Prepare another dewar of trichlorethylene and dry ice. The use of this dewar will be described below.

4. Have a supply of liquid nitrogen available for immediate use and also set aside a small dewar in readiness.

5. Carefully weigh the Hoke tubes which are to be partially filled with NBM C-616. Record these tare weights in the NBM sampling book along with the operator's name, the number of the sample, the date, the number of the Hoke tube, the number of the Harshaw cell containing the material to be used in the sampling, and the lot number of the material in the Harshaw cell. The information concerning the Harshaw cell and the NBM material which it contains is readily obtainable from the white tag fastened to every Harshaw cell of NBM material.

6. Attach the Harshaw cell, if not already in position from previous runs, to connection A.

7. Place a container of hot water nearby.

8. Finally, place the Hoke tubes to be filled during the operation on the system in positions 10-15 (Figure 1). Any number of tubes from one to six can be handled simultaneously. Hoke valves are used for sampling NBM C-616 material as they allow only a small amount of vapor to pass which is very vital in controlling the size of the samples.

9. All samples must weigh not less than 1.0 (one) g. and not more than 5.0 (five) g.

B. Procedure - Assuming the system is now ready for use, operate as follows:

-3-

Operation	Reason for Operation
1. Start vacuum pump.	1. The sampling is a vapor phase transfer carried out in vacuo.
2. Open valves x and y (Kerotest)	2. Valve x connects the pump being used to the pump manifold. Valve y opens the pump to the chemical trap for the NBM system. The chemical trap is the final barrier in the line leading to the pump. Its primary purpose is to protect the pump from HF, C-616, and water vapor by their respective actions upon sodalime, activated carbon, and Drierite. C-216 should never be used in this sort of a chemical trap, because of an explosive compound formed between C-216 and activated carbon.
3. Open Kerotest valve 1.	3. The pump is now evacuating the cold trap of air or other non-condensibles which have collected there. It is to be remembered that the cold trap has been standing for at least fifteen minutes in a dewar of dry ice and trichlorethylene in

order to freeze down the NBM C-616 collected in it. Non-condensibles are materials that will not condense when they hit cold areas. They are often present in the Harshaw cells. The large portion of the non- condensibles is HF and nitrogen.

4. Open Kerotest valve 2.

    4. It opens the cold trap to the main part of the system.

5. Open Kerotest valve 3.

    5. The operator is now opening the remaining valves in the sampling arm of the NBM system to the pump.

6. Open Hoke valves 4, 5, 6, 7, 8, and 9.

    6. These valves lead to the Hoke sample tubes and are the outlets to them from the system proper.

7. Open Hoke tube valves, 10, 11, 12, 13, 14, and 15.

    7. Now the pump is evacuating every section of the NBM sampling arm.

8. Use the oxygen-gas torch to flame all of the tubing that is now being evacuated. Start at valve 2 and work to the Harshaw cell connection flaming every inch. Give especial attention to flaming the Hoke tubes and the U-tube labeled M on the diagram. Move the flame

    8. By flaming the line, water vapor and any stagnant NBM C-616 are cleared from the line. These materials are retained in the cold trap and the chemical trap.

It is advisable to heat from the cold trap toward the Harshaw connection as the pump is then pumping directly on the area being

gradually along the tubing, always following the vapor ring that will form on the tubing just ahead of the flame. It is unsafe to heat the lines so that they become uncomfortable to the touch.

heated by the torch. If the operator, for example, flames the U-tube first and there is some material plugging the line between the U and cold trap, a pressure will be built up.

9. Close valves 3 and 2.

9. The system is now being leak tested. If valve 3 is gas tight, then it is not necessary to close valve 2.

10. Wait for about ten minutes.

10. If after a ten minute wait the gauge still shows a vacuum of about 30 inches Hg, proceed with the sampling. However, if the gauge has dropped during the ten minutes, locate and remedy the leak before continuing. For further procedures in leak testing, see Section C, below.

11. If system is leak tight, open valves 3 and 2.

11. The system is opened to the pump and thoroughly evacuated.

12. Close valves 10, 11, 12, 13, 14, and 15.

12. The Hoke tube valves are closed at this time to prevent any non-condensibles present in the Harshaw from collecting in the tubes.

13. Gradually raise a dewar of dry ice and trichlorethylene up around the U tube M. After approximately 2 inches of the lower portion has been chilled, open the valve on the Harshaw cell connected at A. Collect the NBM C-616 for about 45 seconds - always pumping on the material in the U tube.

13. Before the Hoke tubes receive their samples, it is necessary to build up a supply of material in the U-tube. This material will then be transferred into the Hoke tubes. The C-616 from the Harshaw will condense in the U-tube. The system is open to the pump at all times during this step, the purpose being to effectively conduct a distillation to remove HF and volatile fluorocarbons, since Hoke tube samples should be as free of these substances as possible.

14. After 45 seconds, close the valve on the Harshaw cell.

14. Enough material will have collected in the U-tube by this time.

15. After 2 minutes of additional pumping, close valve 3.

15. All non-condensibles should have been pumped off by this time.

16. Remove the cold dewar from the U-tube and place the container of hot water in position so that the U-tube is immersed in the hot water.

16. The hot water will vaporize the condensed NBM C-616 and the gauge will indicate a pressure rise of about four to five inches of Hg. Usually the gauge reading will go from about thirty to twenty-five inches vacuum.

17. Immerse the lower tip of the Hoke tube about one inch into a dewar of L-28. Open valve 10.

17. The lower tip of the Hoke tube is chilled first so that the vaporized NBM C-616 will go to the bottom of the tube when valve 10 is opened and will not condense and form a plug around the top of the tube.

18. Gradually raise the dewar flask of L-28 completely immersing stem of the Hoke tube for approximately thirty seconds.

18. Experience has shown that usually a sample within the range of 1.0 to 5.0 grams can be collected during this time.

19. Close valve 10 and remove the dewar of L-28.

19. The sample should be in the Hoke tube.

20. Repeat steps 17, 18, and 19 for each Hoke tube; namely, valves 11, 12, 13, 14, and 15.

20. Each tube is filled in the same manner.

21. Open valve 3 and remove the hot water bath from the U-tube.

21. All excess NBM C-616 material left in the U and lines at the conclusion of sampling must be removed to the cold trap.

22. Flame out the system as before; this time do not flame the Hoke tubes which now contain the samples.

22. The flaming is to remove NBM C-616 from the lines. Flame up to the connections between the Hoke tubes and Hoke valves but do not flame the sample bearing tubes.

23. Close valves 4, 5, 6, 7, 8, and 9.

23. This is preparatory to removing the Hoke tubes; therefore the system must be closed to the atmosphere.

24. Close valve 2, open valve 16, and bring the whole system to 1 lb. gauge pressure of dry nitrogen. Remove and weigh the Hoke tubes.

24. The system must be kept dry, and this operation prevents the entrance of moist air.

25. If the sample weight is between 1.0 and 5.0 grams, record the gross and net weights in the NBM log book, and screw the metal plug into the Hoke tube. The operation is complete.

25. It is necessary that a record of each sample be kept. The metal plug which is not a part of the tare weight of the Hoke tube is a precaution taken against the possibility of a valve leak which would allow C-616 to escape.

26. If the Hoke tube does not contain a sufficient amount of material, again place the tube on the system and repeat the operation.

26. In repeating the operation, the L-28 immersion time may need to be changed. This is left to the judgment of the operator.

27. If the Hoke tube contains too much material, again place the tube on the system and pump some of the sample into the cold trap.

27. Hoke tubes containing too much material have been known to burst. Therefore, it is important that tubes are not overloaded. The operator must become more or less

familiar with the system before
he can estimate how long to pump
on a Hoke sample in order to
remove a certain amount of material.

C. Further Procedures in Leak Testing

1. Close valve 2.

2. Open valves 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15.

3. Open Kerotest valve 16.

4. After a gauge pressure of approximately 10 pounds has been built up, close valves 16 and 3.

5. Coat every connection in the sampling system with soap solution.

6. After testing, evacuate the system completely.

1. This is a method using pressure testing, necessitating the isolation of the cold trap and pump from the rest of the system.

2. All sections of the sampling arm must be put under nitrogen pressure.

3. The opening of this valve permits nitrogen to flow into the sampling arm.

4. The sampling arm is now isolated from the rest of the system and is under nitrogen pressure.

5. Bubbles will form at the point where nitrogen is escaping. It is then possible to repair the leak and leak test the system again; if it is then leak tight, continue the sampling operation.

6. This prepares the system for sampling.

This discussion of operational technique finishes the method of NBM, C-616 sampling.

IV. Dumping and Transferring

A. Preparation

1. Connect the cell that contains the material to be transferred at D.

2. Connect the receiver to the system at E.

3. Immerse the cell from which C-616 is being transferred in a container of hot water. Use an electric strip heater to keep the water hot.

4. If the system is being used for transfer purposes, immerse three quarters of the container receiving the material at point E in L-28 and frequently play an oxygen-gas flame on the valve and upper portions of this receiver to keep these parts from becoming clogged with NBM C-616. Heat these parts until heated area feels quite warm to the touch.

5. If the system is used for dumping purposes, connect a large B type cylinder at E and freeze it in a large container of trichlorethylene and dry ice slush.

6. Focus an infra-red heating lamp on the valve of the receiver to keep it from becoming clogged with NBM C-616.

7. As in all dumping procedures, there is a tendency for the non-condensibles to build up over a period of time. When the gauge pressure indicates that this has happened:

(a)   Close valve to the cell being dumped.

(b)   If there is no appreciable drop in pressure when hot
      cell is closed, condensation is not taking place. It
      is then necessary to pump the non-condensibles from
      the lines and the receiving cell.

B.   Procedure

Operation	Reason for Operation
1. Weigh cell to be dumped and record weight.	1. In the case of simple transfers, weigh only the cell to be filled before and after the operation as the operator must keep the sample weight within certain limits. When dumping, record the gross and tare weights of the cell being dumped and enter all pertinent information in the "Dumping Log Book".
2. Attach the cell to be dumped or the source of transfer material to system at D.	2. Self-explanatory.
3. Attach receiving cell at point E.	3. Self explanatory.
4. Go through steps 1-4 as written up in Procedure on Hoke Tube Sampling.	4. Reasons are identical to those already given.

5. Open Kerotest valve 17.

5. This valve opens the remainder of the left arm of the NBM system to the pump so that it can be evacuated.

6. Flame lines with oxygen-gas torch.

6. See reason 8 under Procedure on Hoke Tube Sampling.

7. Close valve 17.

7. The system must be leak tested at this stage. See steps 9 and 10 under Procedure on Hoke Tube Sampling and Section C on "Further Procedures on Leak Testing".

8. If system is leak tight, immerse the cell at D in hot water.

8. The heat will vaporize the solid NBM C-616.

9. If it is a dumping operation, place a container of dry ice and trichlorethylene around the cell at E. If it is a transfer operation, place a dewar of L-28 around the cell.

9. Vapor phase transfers go from hot to cold bodies. The NBM C-616 condenses out in the cold receivers.

10. Open valve on cell containing the NBM C-616 at D.

10. This permits the C-616 vapors to enter the system.

11. Open valve on cold receiver at E.

11. The C-616 will now condense in the receiver.

12. Keep infra-red heating lamp focused on the valve of receivers which are cooled with trichlorethylene and dry ice. Use oxygen-gas torch to keep upper portion and valve of receivers which are cooled with L-28 warm to the touch.

12. The heating insures passage of C-616 through these areas, thus eliminating the possibility of plugging.

13. It is now necessary to pump off non-condensibles as follows:

(a) Close valve on cell D.

(a) Large quantities of C-616 will be pumped into the cold trap unless the source of 616 is closed.

(b) With valves 2, 1, and E open, open valve 17.

(b) The vacuum pump can now pump the non-condensibles from the system

C. Closing Down the System

1. In order to calculate the approximate rate of transfer from the hot to the cold cell, remove the receiving cell now and then and weigh it. When the correct amount has been transferred or the hot cell is empty, the system is turned off as follows:

(a) Close valves on cells at D and E.

(a) Both cells are under vacuum and it is imperative that they remain so after they are taken from the system.

(b) Open valve 17, flame the lines, and pump on the system.

(b) Reason given before.

(c) Close valve 2. Open valve 16 and fill the system with nitrogen to 1 lb. gauge pressure. Close valve 17. Close valve 16.

(c) The pump must be isolated from the system before the system is brought to atmospheric pressure.

(d) Remove dewar and hot bath and disconnect the cells at D and E.

(d) Self explanatory.

(e) Screw flare plugs into connections at D and E.

(e) This keeps the lines free from atmospheric moisture.

(f) In order to shut down the system, close valves in the following order: 17, 2, 1, y, x and switch off pump.

(f) Logical order to follow.

(g) Open Calif. valve Z.

(g) This operation permits air to go into the pump and it will prevent the oil in the pump from diffusing into the system.

(h) After the "hissing" of air entering the pump has stopped, close valve Z.

(h) The pump is now under atmospheric conditions as it should be when it is not in use.

(i) Enter all data in the correct NBM book.

(i) Self explanatory.

The operation is now complete.
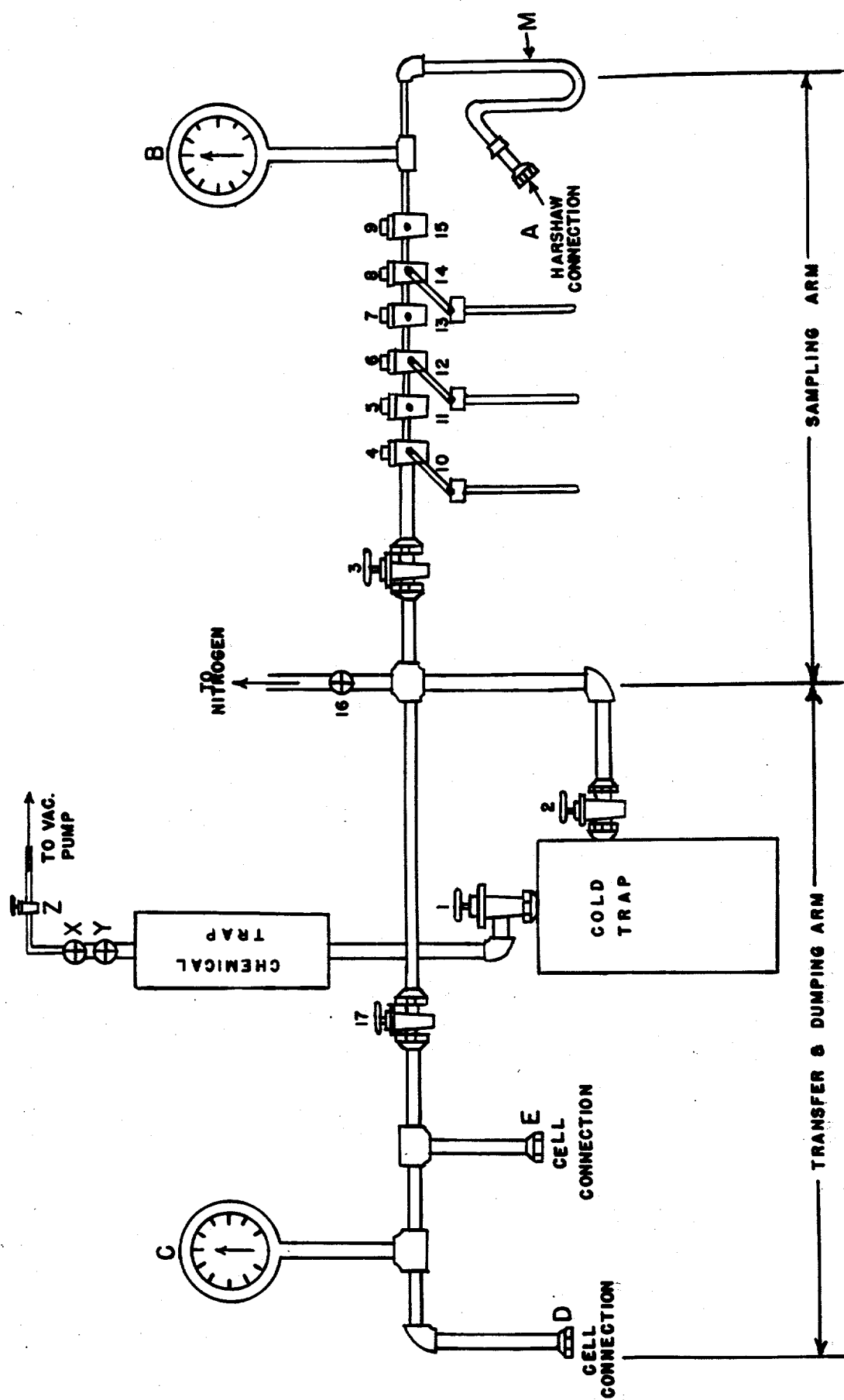
FIGURE 1
NBM SYSTEM

-1-

DBM DUMPING SYSTEMS

I. Purpose

The purpose of this system is to transfer C-616 from small containers such as are used in the laboratories to larger cylinders which are eventually returned to the Process Area.

II. Operation

The C-616 is transferred in the vapor phase by means of the system shown in Figure 1.

The proper techniques of operation are the same as those given in the procedure "NBM Sampling and Dumping".

III. Precautions

As in any system involving transfer of C-616, the operator must wear safety glasses. It is also advisable for operator to wear leather gloves to protect hands against valve handles and dry ice.
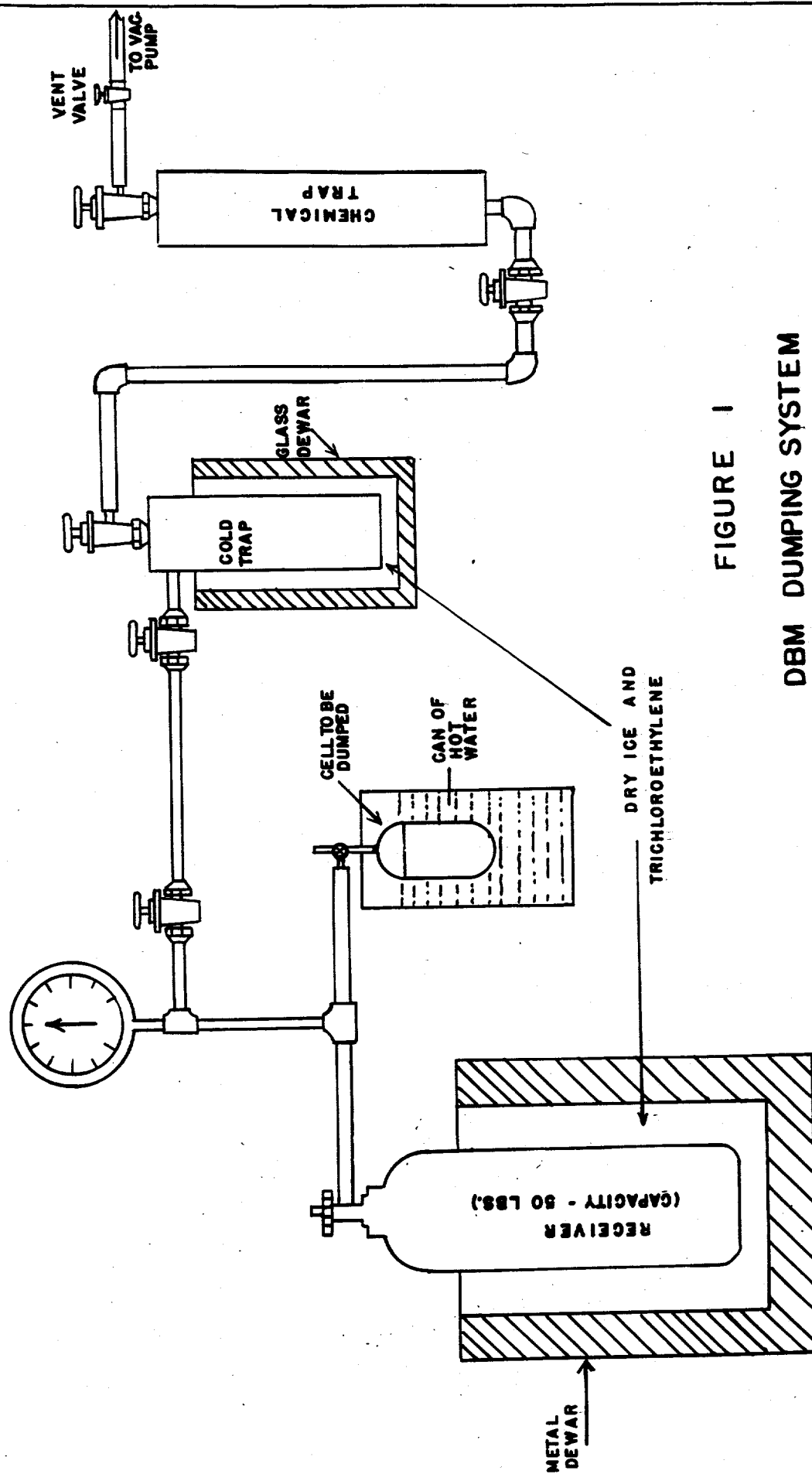
FIGURE 1

DBM DUMPING SYSTEM

3.6

C-616 SAMPLING IN THE 600 BUILDING

I. Preparation

1. Get permission to take a sample from the building foreman.

2. Get foreman to start Stokes pump.

3. Plug in nichrome resistance heater.

4. Check valves A and A_1. They should be closed with torque wrench set at 65 lb.

5. Check valve N. It should be closed with torque wrench set at 45 lb.

6. Open valves V, B, C, D, and F in order.

7. When vacuum gage I reads 29 inches, close valve C.

8. Immerse cold trap K in L-28.

9. Plug in Pirani gage.

10. Start vacuum pump.

11. Open valves E, H_1, and H, and evacuate system to a pressure of 50-75 microns.

12. Close valve C.

II. Procedure

1. Close valve V with torque wrench set at 65 lb.

2. Open valve A or A_1 (depending upon line to be sampled) and let pressure on gage L rise to 1 atmosphere.

3. Close A or A_1 and open valve V. This purges line to valve C.

4. With Pirani gage reading of 50-75 microns. Close valve E.

5. Close valve V with torque wrench set at 65 lb.

6. Close valve G.

7. Crack open valve A or A_1.

8. Slowly open valve C.

9. When gage I reads 25 inches vacuum, close valve C.

10. Close valve A or A_1 with torque wrench set at 65 lb.

11. Open valve V.

12. Close valves H and H_1.

13. Open valve C and evacuate manifold to not less than 28 inches of vacuum.

14. Close valve C and open valve G.

15. After one minute, open valve E and read pressure on Pirani gage.

16. When pressure reading on Pirani is less than 100 microns, close valve D and remove sample cylinder. Repeat for duplicate sample.

17. Tag cylinder giving date, time, source, purpose of sample, and sampler's name.

18. Close all valves, disconnect heater, pump, and Pirani gage. Remove L-28 from trap K.

19. Send samples to Laboratory A.
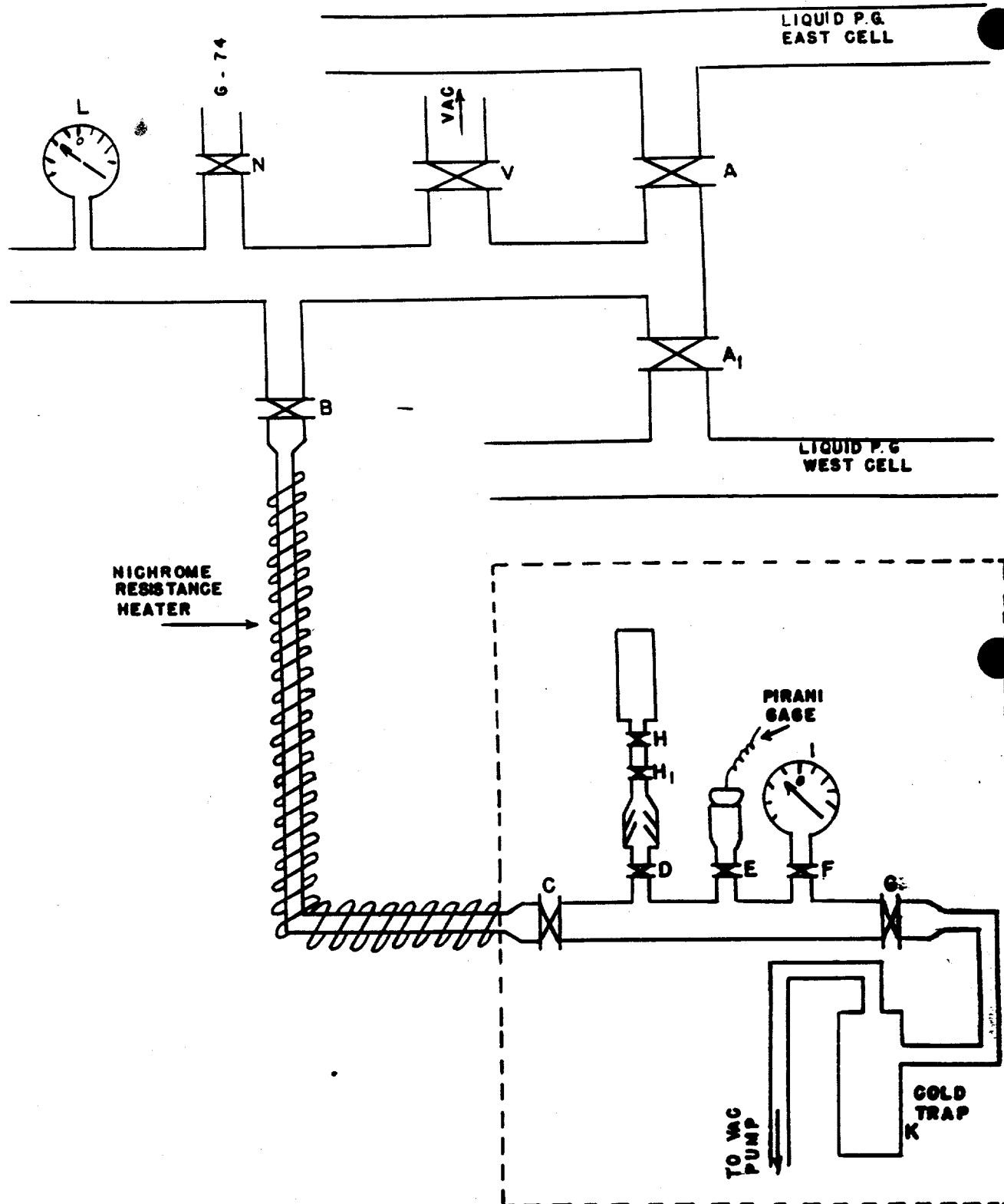
FIGURE I

C-616 SAMPLING IN 600 BLDG.

DETERMINATION OF C-616 IN G-74

Part A

Sampling

This method is for the determination of C-616 in G-74. Part A includes directions for taking the gas sample into the 5 liter bulb; Part B includes directions for the solution of C-616 in water and the determination of the TO_2^{++} ion colorimetrically; Part C includes directions for the volumetric determination of the TO_2^{++} ion.

I. Apparatus

    A. Sample Bulb - Five liter bulbs fitted with adapters as shown in Figure 1 are required. Cases are provided for the transportation of the bulbs.

    B. Sampling Buggy - The sampling buggy shown in Figure 2 is used to take samples.

SOME DO'S AND DON'TS ON THE CARE OF THE BUGGY

1. Don't move a buggy if the lines are evacuated.

2. Do open the valves to admit air into the manometer before moving.

3. Don't fail to take a leak rate on all connections before sampling.

4. Don't use Apiezon-Q to stop a leak; however, it may be used to find a leak.

5. Do your best to stop leaks by tightening the couplings.

6. Don't remove a stuck pump and install a new one.

    NOTE: A buggy with a stuck pump shows that the trap is exhausted.

7. Do return buggies with stuck pumps to Works Laboratory Field Office, 303-10, for repairs.

8. Use two wrenches for tightening flare fittings.

   NOTE: Use of only one wrench may twist the tubing or break the buggy manifold.

9. Don't open the manometer to a vacuum quickly, as this may pull mercury into the lines.

10. Don't bend the copper tubing leading from the buggy to the sampling point. Disconnect it completely when moving a buggy.

II. Procedure

   A. Testing buggy for leaks (This procedure should be carried out whenever buggy is used. As a rule no leaks will be found and the procedure will not take but a few minutes). WHEN OPERATING BUGGY AND GLASS BULBS ARE UNDER VACUUM, SAFETY GLASSES MUST BE WORN.

      1. Close all valves.

      2. Connect the buggy to sampling point and plug in pump cord on 110 volts A.C.

      3. Start vacuum pump. Open valve E.

      4. Open valve B slowly, taking care that no mercury is pulled into the line from the manometer. Allow system to pump until the pressure is less than 5 mm. absolute.

      5. Close valve B and watch manometer for evidence of leaks.

         (a) If there is a leak, close valve E, and watch manometer for indications of a leak. Indications of a leak here show that the connections to the manometer are not tight. Tighten carefully, if leak does not stop get a new buggy and return the old buggy to Works Laboratory Field Office, 303-10, for repairs.

(b) If closing valve E stops the falling off of the manometer, check valves A, C, C[1], and D. Open valve E again and see if the leak was due to a valve which may have been opened slightly. If there is still a slight leak or if there was not any leak at the beginning, proceed with the following testing.

6. Open valves D and B and evacuate the purge bulb.

7. Close valve B and watch manometer for indication of leaks.

(a) If there was a leak indicated in (b) of step 5, and no indication of a leak at this point, then valve D leaks through the seat. Make a notation of this, if leak was very small (5 mm. per minute or less), the buggy can still be used. If there is still a leak, but it is much _slower_, indications are that valve D and the purge bulb are not leaking.

(b) If there was not a leak before and there are indications of a leak now, the bulb leaks and the buggy should be sent to Works Laboratory Field Office, 303-10 for repairs.

(c) If there are not any leaks, proceed with step 8.

8. Close valve D, open valves A and B making sure that the valves on the line recorder manifold or other sampling point are closed.

9. Close valve B and watch manometer for leaks.

(a) If there was a leak in step 5 (b) and there is none now, valve A leaks through the seat. Make a notation and report the fact to the supervisor. The buggy can still be used.

(b) If there was a leak in step 5 (b) and there is still about the same leak, proceed with step 10. If the leak seems greater, tighten the flare fittings and check the valves on the sampling point. Proceed with step 10.

10. Close valve A and attach bulbs to fitting above valves C and C^1. Make sure the stopcocks and the spherical joint are well greased with MFI grease.

11. Open valves C, C^1 and B, evacuating the short lines between valves C, C^1 and the stopcocks on the bulbs.

12. Close valve B and watch manometer for leaks.

(a) If there was a leak indicated in step 5 (b) and no leak now, then either valve C or C^1 leaks through the seat. Close both valves and open the stopcock on the bulb over valve C. If there is a leak through the valve C it will show on the manometer. If there is not a leak through valve C, open the stopcock on the bulb over valve C^1. If there is a leak through this valve, it will show on the manometer.

(b) If there was a leak indicated in step 5 (b) and it continued whether valves C and C^1 were opened or closed,

it can be assumed that the buggy manifold is at fault.
If this is the case, take the buggy to Works Laboratory
Field Office, 303-10, for repairs.

(c) If no leaks were found in all 12 steps, the buggy is
ready to take a sample.

(d) If there was a leak in Step 9 (c) isolate it in the
following manner: Disconnect the tube from the sampling
manifold at the manifold and plug up the end of the
copper tube with a rubber stopper. Open A and B,
close valves C, C^1 and D, and evacuate the line. Then
close valve B and watch manometer for a leak. If there
is a leak, tighten the flare fitting connecting the
copper line to the buggy. If this does not stop the
leak, close valve A, disconnect the copper line and
check the flare for cracks. If there is not a leak,
connect the line back to the sampling manifold after
first looking for a defective flare at this joint. Then
evacuate the line, close valve B and watch the manometer.
If there is still a leak, use some Apiezon-Q over the
flare fittings. If this stops the leak, tighten the
flare connections and remove the Apiezon-Q. If this
does not remove the leak, the valve on the sampling
manifold is at fault. Notify the supervisor of this
fact. If the system is now tight, the sample may be
taken.

B. Procedure for taking C-616 Sample

1. Open all valves except the valve on the sampling manifold.
   NOTE: When set up at a line recorder station, open the valve on the sampling manifold, but be sure the valve on the loop is closed. Check with line recorder operator.

2. Let the system come to equilibrium. This requires 5-10 minutes.

3. Read the manometer, (both sides if it is a U-tube), record the pressure (if the manometer is a U-tube, record the difference). This is the starting pressure.

4. Close valves C, C^1 and D. If this is the first sample taken at the station, have the operator open the valve to the cell for 10 to 15 seconds and purge the line through the trap. Then close valve B, open valve D and have operator open sampling valve. This purges the line into the metal bulb.

5. When pressure reaches equilibrium, about 1-2 minutes, close valve D and open valve C or C^1 and allow gas to fill bulb.

6. Close valve A and read the pressure on manometer (difference between both sides of U-tube). This pressure subtracted from the starting pressure will give the pressure of the sample.

7. Close stopcock on bulb.

8. Have operator close sampling valve.

9. Open valve A, B and D and evacuate.

10. Close valve C or C^1, whichever one was opened.

11. Remove bulb, fill out tag recording pressure, temperature and volume.

12. If the concentration of C-616 in the gas is very low (less than 0.01 mol. per cent) mark the label EVAP. in red crayon. Check with supervisor in case of doubt.

13. Tie tag to bulb, put bulb into the box and have it taken to Room 105, Laboratory B.
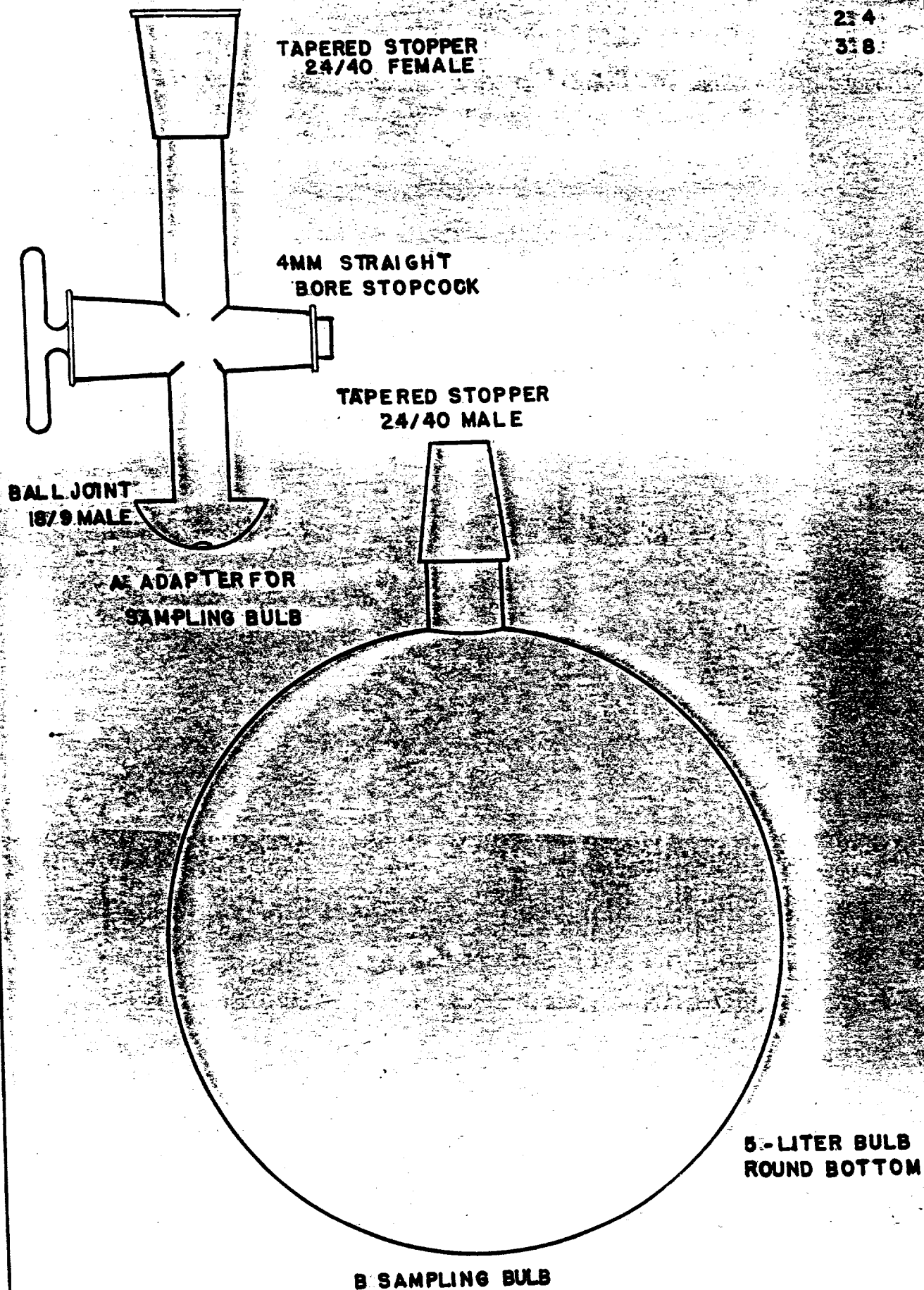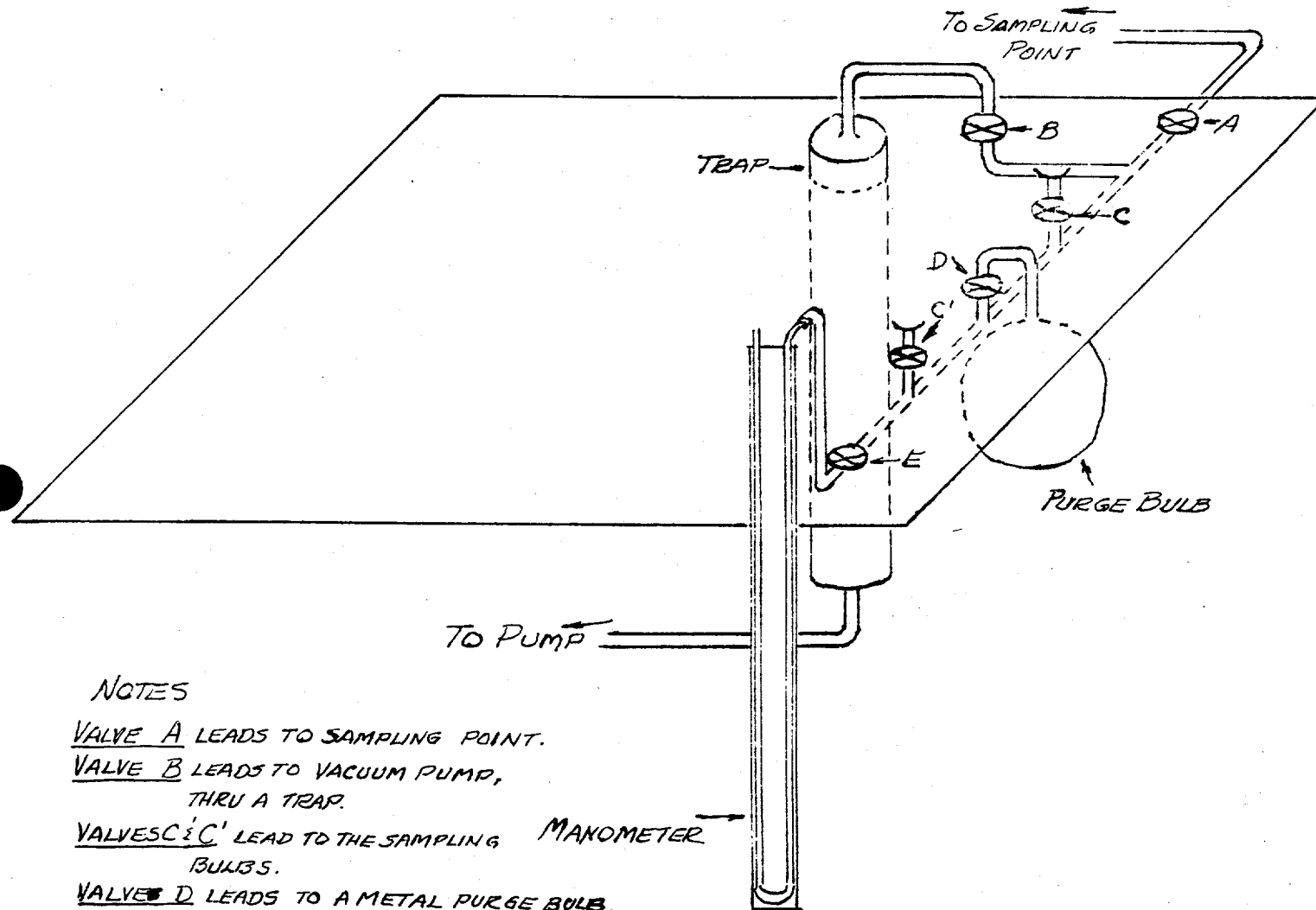
FIGURE I

FIGURE 2

WORKS LABORATORY SAMPLING BUGGY

TO SAMPLING POINT

TRAP

B

A

C

D

C'

PURGE BULB

E

TO PUMP

MANOMETER

NOTES

VALVE A LEADS TO SAMPLING POINT.

VALVE B LEADS TO VACUUM PUMP, THRU A TRAP.

VALVES C & C' LEAD TO THE SAMPLING BULBS.

VALVE D LEADS TO A METAL PURGE BULB.

VALVE E LEADS TO THE MANOMETER

HRB 9-17-45

PROCEDURES FOR OBTAINING SAMPLES FROM TANKS

(Read thoroughly and carefully)

For All Water Tanks -

There are normally five water tanks in operation (H-303-B, H-303-C, H-304, H-304-C, and H-308). Samples are obtained from these tanks in wide-mouthed pint bottles. WEAR RUBBER GLOVES while taking samples from hot water tanks H-304, H-303-B and H-303-C. Determine turbidity and pH of these samples. Record the results of these determinations on the report sheet.

For Water Filters -

Use wide-mouthed pint bottles to obtain samples from water filters. Three samples are to be taken from the filters. A sample of the water that enters the filters is taken from the line running into the hopper in the center of the filtering apparatus. A sample of the water leaving each filter (both #1 and #2) is taken from the pilot valves located on each filter. (Consult the filter operator or the chief chemist to find the location of these valves). Determine turbidity on these samples and record results on the report sheet.

Note: If sanitary water is being used in place of filtered water, only one sample is necessary. Obtain this sample in a wide-mouthed bottle from the pipe line entering the top of the large reservoir tank adjacent to the filters. Determine the turbidity of the sample and record the result on the report sheet.

For Acid, Alkali, and Ammonia Tanks -

The sample for these tanks (H-303, H-304-A, H-304-B, H-305, H-307 and H-303-A) will be taken in glass-stoppered bottles. The bottle is placed in the wooden holder and secured by means of the wooden pin and the wire. The glass stopper is removed and the bottle lowered into the tank. Rinse the bottle in the solution several times. Take equal amounts of the sample from the center and both ends of the tank. Do not take sample from only one end of the tank. Replace the stopper when the bottle is almost filled and rinse in a water tank before removing bottle from wooden holder.

Precautions:

1) ALWAYS WEAR YOUR GOGGLES WHEN TAKING SAMPLES FROM THESE TANKS.

2) If the sample is hot, rinse in a HOT water tank. DO NOT RINSE IN A COLD WATER TANK! The bottle may break and shower you with hot acid or alkali! If the sample is cold, rinse in a cold water tank for the same reason.

3) IF ANY LIQUID FROM ANY OF THESE TANKS FALLS OR SPLASHES ON YOUR SKIN OR CLOTHING, WASH IT OFF IMMEDIATELY WITH LARGE AMOUNTS OF WATER FROM A COLD WATER TANK.

DETERMINATION OF MFL MIST

Part A

SAMPLING

This is a method for the determination of MFL mist in pump dis-charge after passing through a mist filter.

Part A describes the method for taking the sample into a 5 liter monel can.

Part B describes the method for the gravimetric determination of MFL in the can.

Part C describes the determination of MFL in the can by infra-red absorption.

I. Apparatus

A. Sample cans

The samples are taken in 5 liter monel cans fitted at each end with one inch gate valves packed with D-29 (See Figure 1).

B. Sampling system

The sampling system used is shown in Figure 2. All lines are one inch monel pipe. The can is attached to the system by dresser couplings and is enclosed in an oven so that it may be heated to the temperature of the gas at the discharge of the pump. (About 120° F.).

II. Procedure – The procedure will be described on the assumption that the can is in place and has had time to heat to the temperature of the oven. If there is no can in place, install one following the directions in step L and allow the can to heat for at least one hour.)

A. At start have valve 5 open and all other valves closed.

B. Record oven temperature.

C. Open valves 1 and 2 (on opposite ends outside of oven).

D. Open valves 3 and 4 (valves on mist can).

E. Close valve 5 (main line valve).

F. Allow gas to run through sample can for sixty (60) seconds.

G. Open valve 5.

H. Close valves 3 and 4.

I. Close valves 1 and 2.

J. Remove sampling can by raising oven, unloosening bolts on dresser couplings and sliding sleeve toward the can. The can should now come out and the couplings can be removed.

K. Tag can with time and temperature and pressure of sample and send to Room 105, Laboratory B for analysis.

L. Install new can. In replacing couplings make certain that the rubber gaskets on both ends of each sleeve are in place and that the sleeves are not placed too far toward the can (the bolts cannot be tightened) or too near the support (the oven will not fit on properly).

M. After the can is in place and securely fastened, lower the oven so that it fits snugly and insert the thermometer in one of the holes provided.

1" GATE VALVE PACKED WITH D-20

1" MONEL PIPE

SILVER SOLDER

5L MONEL CAN

SILVER SOLDER

1" GATE VALVE PACKED WITH D-20

1" MONEL PIPE

FIGURE 1

SAMPLE CAN FOR MFL MIST ANALYSIS

TO
RECOVERY
SYSTEM

DRESSER
COUPLING

OVEN

MIST SAMPLE
CAN

DRESSER
COUPLING

2

4

5

3

1
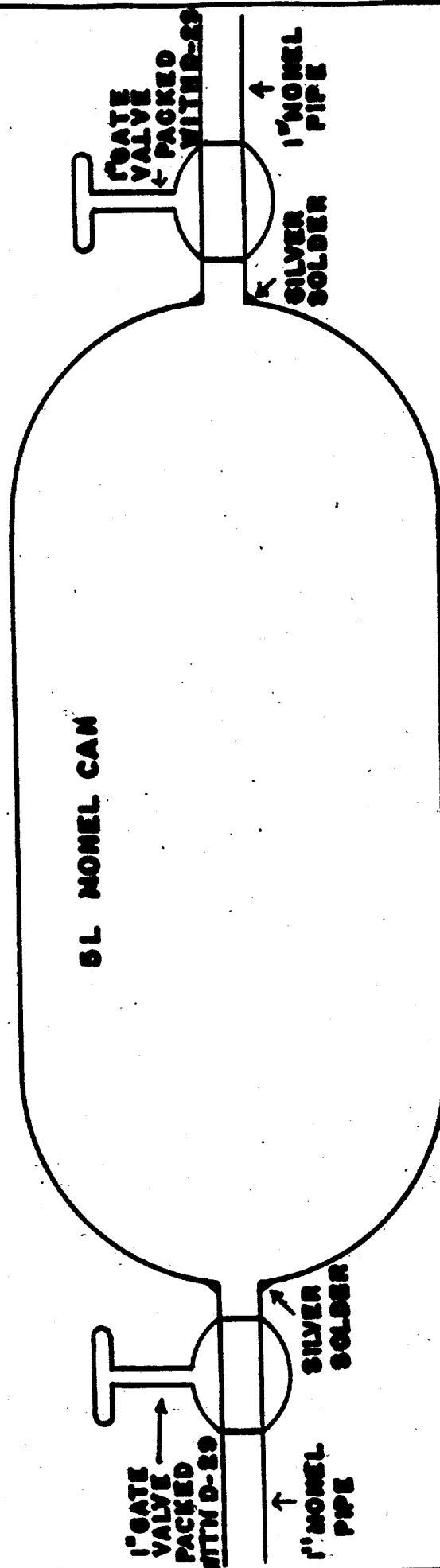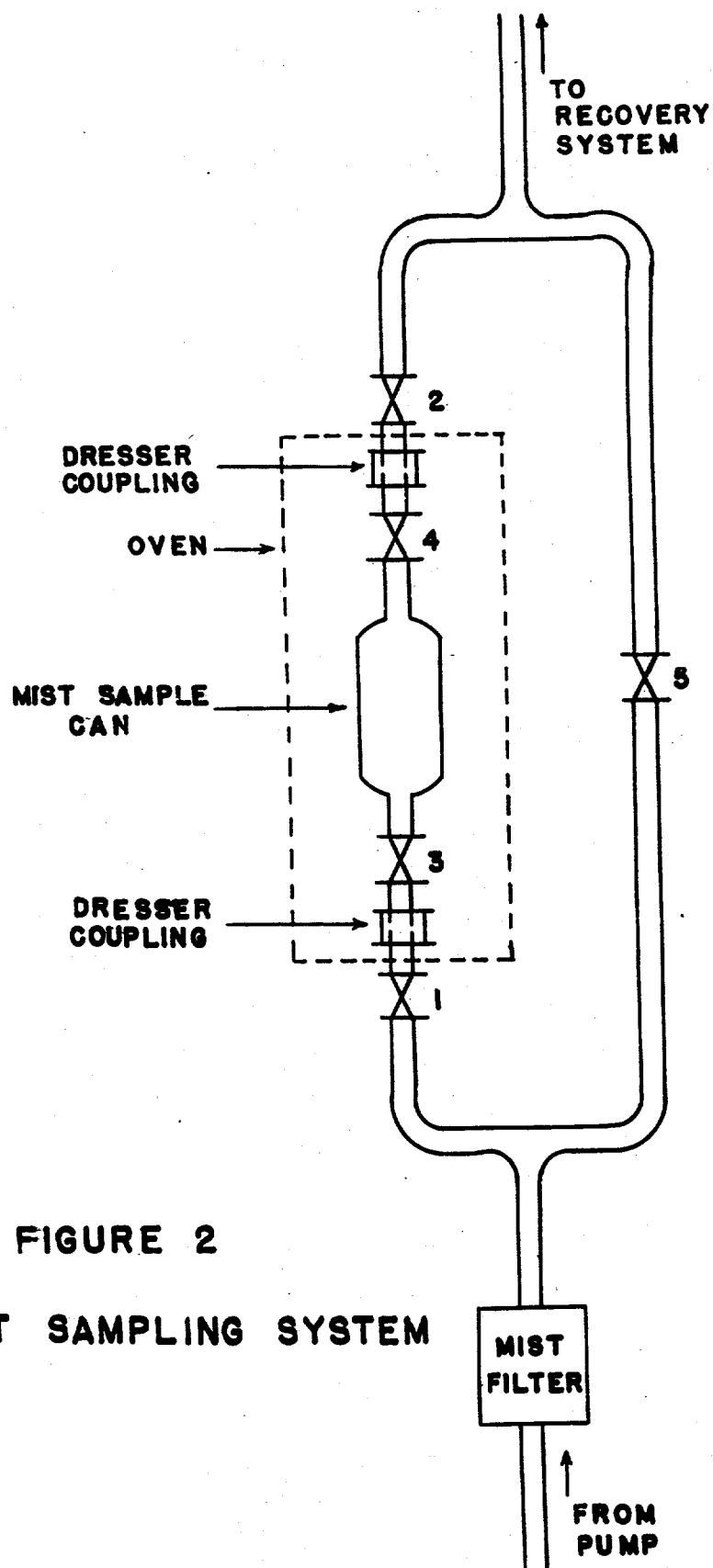
FIGURE 2

MIST SAMPLING SYSTEM

MIST
FILTER

FROM
PUMP

REAGENTS REQUIRED IN 1301 BUILDING ANALYSES

1. Sodium Hydroxide (0.1 N)

Weigh out about 4.5 grams of analytical reagent grade NaOH (pellet) on trip balance, dissolve in 100 ml. of distilled water, and dilute to one liter.

Standardization: Dry about 10 grams of primary standard analytical reagent grade potassium acid phthalate in an oven for at least two hours. Weigh accurately approximately three 0.9 gram portions of the potassium acid phthalate on an analytical balance. Treat each portion in the following manner: Dissolve the potassium acid phthalate in about 50 ml. of CO_2 free water in a 250 ml. Erlenmeyer flask. Add 5 drops of phenolphthalein indicator and titrate to a pink color with the 0.1 N NaOH.

Calculation:

$$N\ NaOH = \frac{grams\ potassium\ acid\ phthalate}{(ml.\ NaOH)\ (0.2041)}$$

2. Sulfuric Acid (0.3 N)

Measure from a small graduate 9 ml. of concentrated H_2SO_4. Add to 200 ml. of distilled water and dilute to 1 liter.

Standardization: Measure 50 ml. of the standardized 0.1 N NaOH solution from a burette (Or pipette) and titrate with the 0.3 N H_2SO_4 using phenolphthalein as an indicator. At least three titrations should be made.

Calculation:

$$N\ H_2SO_4 = \frac{(N\ NaOH)\ (ml.\ NaOH)}{ml.\ H_2SO_4}$$

3. Phenolphthalein Indicator

Dissolve 1 gram of phenolpthalein in 50 ml. of 95% alcohol and add 50 ml. of distilled water.

-2-

4. Sodium Thiosulfate (0.1 N)

Dissolve 25 grams of analytical reagent grade $Na_2S_2O_3 - 5 H_2O$ in water. Add 2 grams NaOH and dilute to one liter.

Standardization: Prepare a 0.100 N potassium dichromate solution as follows: Dry about 10 grams of finely ground analytical reagent grade $K_2Cr_2O_7$ in an oven at 110° C. for at least two hours. Weigh out 4.903 grams of the dried salt, dissolve in distilled water and dilute in a volumetric flask to one liter with distilled water.

Dissolve 2-3 grams of KI in 200 ml. of distilled water and add 10 ml. of 1:1 HCl. Measure accurately from a burette into a glass stoppered flask containing the KI solution 30-40 ml. of the potassium dichromate, and allow to stand for a period of 5-10 minutes. Titrate with the 0.1 N $Na_2S_2O_3$ solution until the solution is light yellow. Add 2-3 ml. of starch indicator and titrate to the disappearance of the blue starch color. (A slight green color will remain).

Calculation:

$$N\ Na_2S_2O_3 = \frac{(ml.\ K_2Cr_2O_7)\ (0.100)}{ml.\ Na_2S_2O_3}$$

5. Starch Solution

Mix 5 grams of soluble starch thoroughly with a little distilled water. Pour with constant stirring into 500 ml. of boiling water. Allow the solution to cool and add 10 grams of KI.

6. Sodium Hydroxide (5%)

Dissolve 50 grams of NaOH in one liter of distilled water.

7. Acetic Acid (6N)

Dilute 344 ml. of glacial acetic acid to 1 liter with distilled water.

ANALYSIS OF ELECTROLYTE FOR HF

This is a method for the determination of HF in KF electrolyte.

The acid is titrated with standard NaOH solution.

I. Apparatus

 A. Two copper (or preferably Pt.) plates.

 B. Dipping spoon or rod.

 C. Desiccator (filled with $CaCl_2$).

The operator should be equipped with the following safety equipment while taking a sample: rubber gloves, safety glasses, and face shield.

II. Reagents

 (For preparation, see reagent section. Number refers to solution number in reagent section).

 A. 0.1 N NaOH (1) Standardize accurately with potassium acid phthalate.

 B. 0.3 N H_2SO_4 (2) Standardize against the above NaOH solution.

III. Procedure

 A. Notify the shift foreman when a sample will be taken so cell can be shut down. DO NOT ENTER GENERATOR ROOM UNTIL RED LIGHT IS OFF.

 B. Open sampling valve on top of generator. Allow plenty of room for "blow out" should one occur.

 C. Place sampling spoon or rod in valve opening and agitate in an up and down motion.

 D. Quickly withdraw sampling rod and place small portion of melt on copper plate. (About 0.25 g. of melt should be taken).

-2-

E. Immediately place plates in desiccator.

F. Withdraw a duplicate sample in the same manner.

G. Remove one copper plate from the desiccator and weigh quickly. If necessary, chip off parts of melt. The weight of the sample should be between 0.239 g. and 0.249 g. (Care must be taken to weigh quickly because of the hygroscopic nature of the sample). Transfer the sample to a titration flask containing 50 ml. of 0.1 N NaOH measured from a burette, and reweigh the copper plate.

H. Add 3-4 drops of phenolphthalein as an indicator. If the solution is not red add more 0.1 N NaOH from a burette and titrate with 0.3 N H_2SO_4.

I. Duplicate analyses should be run.

IV. Calculations

$$\% \text{ HF} = \frac{(\text{ml. base x N-ml. acid x N) (20) (100)}}{(\text{wt. sample in g.) (1000)}}$$

The precision of the method should be $\not< 0.2$ per cent.

TESTING RESISTANCE OF ANODES

This is a method for testing the resistance of carbon anodes used in the C-216 generators. The resistance is measured with a resistance meter.

I. Apparatus

Resistance meter - Leeds and Northrup meter No. 5430-A or other similar instrument should be used.

II. Procedure
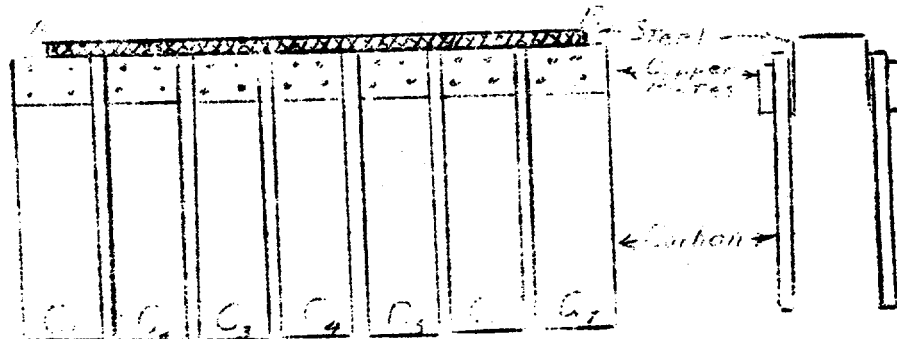
A. Measure the resistance between the base of the anode post (A) and position C_1, C_2, C_3, and C_4.

B. Change one connection to position B and measure resistance to C_4, C_5, C_6, and C_7. AC_4 should equal BC_4.

C. Measure resistance of leads.

D. The resistance of any carbon must be less than 0.016 to 0.020. ohms. Resistance of C_1 = AC_1 - resistance of lead.

E. If a resistance of 0.016 or more is found the carbon must be replaced.

F. Tests are necessary before placing new anodes in generators and when old ones are removed. Carbons on both sides of anodes must be tested.

ANALYSIS OF SEAL POTS FOR H₂SO₄

This is a method for the determination of H_2SO_4 in Seal Pots by titration with standard NaOH.

I. Reagents - (For preparation, see the reagent section. The number refers to solution number in reagent section).

0.1 N NaOH (1) Standardize accurately against potassium acid phthalate.

II. Procedure

A. Open valve on pot and drain out about 15 ml. (Wear a face shield and rubber gloves in this operation).

B. Take a 5 ml. sample dilute to 500 ml. and take a 10 ml. portion of the diluted solution and titrate with 0.1 N NaOH using phenolphthalein as indicator.

III. Calculation-

$$\text{Per cent purity } H_2SO_4 = \frac{(\text{ml. NaOH}) \ (N) \ (0.049) \ (100) \ (50)}{(5) \ (1.87)}$$

DETERMINATION OF HF IN ABSORBER TRAYS

This is a method for the determination of HF in NaF absorber trays by titration with standard NaOH.

I. Reagents - (For preparation, see reagent section. Number refers to solution number in reagent section).

A. 0.1 N NaOH (1) Standardize accurately against potassium acid phthalate.

B. 0.3 N H_2SO_4 (2) Standardize accurately against the above NaOH solution.

II. Procedure

A. Take representative sample from a larger representative sample taken from every other tray.

B. Weigh a sample (about 0.2 g.) into 50 ml. of 0.1 N NaOH. Add phenolphthalein. If the indicator does not turn red add more NaOH from a burette until it does.

C. Heat to 90° C.

D. Back titrate with 0.3 N H_2SO_4.

III. Calculations

$$\text{Per cent HF} = \frac{[(\text{ml. NaOH} \times N) - (\text{ml. } H_2SO_4 \times N)] (0.020) (100)}{\text{wt. sample}}$$

ANALYSIS OF C-216 FOR HF, O_2 AND G-74

This is a method for the determination of impurities in C-216.
The C-216 is converted to Cl_2 and is determined by absorption in NaOH
and iodometric titration. The HF is absorbed on NaF and titrated. The
O_2 is determined by absorption in pyrogallol after removal of the HF
and C-216. The inerts are determined by difference.

I. Apparatus

A. The apparatus used is shown in Figure 1.

B. Asbestos gloves and safety glasses must be worn while the gas
is being sampled.

II. Reagents

(For preparation see reagent section. Number refers to solution
number in reagent section).

A. NaF pellets - Use special reagent grade 1/8" NaF pellets
supplied by the Harshaw Chemical Co.

B. NaCl - Use granular reagent grade NaCl dried for 24 hours at
120° C.

C. NaOH 5% - (6) Dissolve 50 g. of NaOH in 1 liter of distilled
water.

D. 0.1 N NaOH - (1) Standardize accurately with potassium acid
phthalate.

E. 0.3 N H_2SO_4 - (2) Standardize against 0.1 N NaOH.

F. 0.1 N $Na_2S_2O_3$ - (4) Standardize accurately with 0.100 N
$K_2Cr_2O_7$ solution.

(G) 6 N Acetic Acid - (7) Dilute 344 ml. of glacial acetic
acid to 1 liter with distilled water.

III. Procedure

A. Fill tube 5 with 10 g. of NaF pellets and hold in place with
nickel or monel screen. Dry the tube thoroughly in oven before use.
Place clean evacuated sampling bulb in line. Fill absorber 10 with
250 ml. of 5% NaOH, and put tube 5 in place in the line.

B. Sampling is done from three points. They are: (1) In the
absorption room (a) before HF absorber (b) after HF absorber: (2)
On storage tank (there is also a third valve immediately off the
generator but this is used very infrequently). In Figure 1 A and B,
valve 1 represents the valve on the sampling line. Attach flare
connection of sampling manifold to sampling point. (The type of
sampling connection will depend on whether the absorber or storage
tank is being sampled. If the absorber is being sampled use the
valving system shown in A of Figure 1. If the storage tank is being
sampled use the valving system shown in B of Figure 1). Attach the
analysis apparatus C to the end of the sampling connection.

C. If sample is taken of absorber, open valve 1 and 2 and con-
tinue with section D. If sample is on storage tank, close valve 2',
open valve 1 about 1/8 turn and open valves 3 and 4 just enough to
get a flow of gas. (Test flow of gas with splint to determine rate
of flow. The flow should be such that the splint is barely ignited.)
Close valve 4 and open 2', continue with Section D.

D. Open 7 immediately after 2 or 2' is opened. Stopcocks 8 and 9 are closed to all directions. If the absorber is being sampled the pressure of the gas in the system is just slightly above atmospheric (about 1 inch of water) so an aspirator is needed. Adjust 11 so that the flow is approximately 5 liters per hour. (Some experimenting may be required to get this gas rate since it is hard to regulate flow through a fritted glass disk). If the storage tank is being sampled the pressure will be about 30 p.s.i.g. so no aspirator is needed. The flow should be regulated by adjustment of valve 3.

E. Allow gas to flow for 15 minutes. Open stopcocks 8 and 9 and purge stopcocks into side arm. Be careful not to introduce any gas into the bulb at this point.

F. Close 7 and purge side arm for 5 minutes. Open 7 and close 8 and 9 to everything. After a minute SLOWLY open 8 to line and allow gas to be drawn in; care must be taken that the liquid in 10 IS NOT SUCKED BACK.

G When gas starts to flow at normal rate, open 9, close 7 and purge for 45 minutes. To shut down the run the following procedures are used:

(a) If the absorber is being sampled: Close stopcock 9, then stopcock 8 and at the same time adjust 11 so liquid does not rise in bubbler.

Break connection from bulb after stopcock 9, open 11, and close valve 1.

-4-

(b) If the storage tank is being sampled: Close stopcock 9, then stopcock 8, open 7, close 1, and then close 7 when bubbling stops.

H. Remove bulb, close clamp 12. Remove tube 5 and put a cap on tube 6.

I. HF determination - In a neutral mortar add from a burette 50 ml. of 0.1 N NaOH. Add 5 drops of phenolphthalein as indicator. Empty contents of tube 5 into NaOH. Macerate thoroughly and back titrate with 0.3 N H_2SO_4. Occasionally more caustic must be used. Run a blank on the pellets. The blank is usually negative. Liters

$$\text{HF (at STP)} = \frac{(22.41)(\text{ml. NaOH} \times N - \text{ml. } H_2SO_4 \times N)}{1000}$$

J. Cl_2 Determination (C-216) - Dilute contents of flask 10 to 500 ml. and take a 10 ml. sample. Add 4-5 g. KI and 15 ml. of 6 N HAc. Titrate from brown to colorless with 0.1 N $Na_2S_2O_3$.

$$\text{Liters } Cl_2 \text{ (at STP)} = \frac{(22.06)}{(2000)} (\text{ml. } Na_2S_2O_3) (N\ Na_2S_2O_3) (50)$$

To this value must be added the volume of Cl_2 found in the bulb.

K. Determination of O_2 and G-74. - This portion of the analysis is extremely vulnerable to error; therefore, great care must be exercised in carrying it out.

Allow temperature of the bulb to come to room temperature and then equalize the pressure by opening the stopcock to atmosphere momentarily. Attach a leveling bulb to one stopcock and fill with 5% NaOH. Open stopcock to side arm and allow some NaOH solution to pass from leveling bulb into side arm to remove bubbles from tubing. Then allow NaOH to flow into the bulb. Shake until there is no change in volume. Connect

other stopcock of bulb to orsat, purge orsat line with G-74 and pass gas into orsat. Read volume of gas in orsat (designated as "orsat sample"). If volume of gas is small make up to approximately 30 ml. with G-74 (designed as "diluted volume"). Absorb O_2 in alkaline pyrogallol and note orsat reading.

Diluted volume - orsat reading after pyrogallol = ml. O_2

$$\text{Ml. } O_2 \text{ (at STP)} = \text{(ml. } O_2) \frac{(P-P_{H_2O})\,(273)}{(760)(T)} \tag{3}$$

Orsat sample - ml. O_2 = ml. G-74

$$\text{Ml. C-74 (at STP)} = \text{(ml. C-74)} \frac{(P - P_{H_2O})\,(273)}{(760)\quad(T)} \tag{4}$$

$$\text{Ml. Cl}_2 \text{ (at STP)} = \left[(\text{Vol. bulb} - \frac{P-P_{H_2O}}{P} (\text{orsat sample})\right] \frac{(P)}{(760)} \frac{(273)}{(T)} \tag{5}$$

This volume of Cl_2 must be added to volume found in part 9 (Equation 2).

P = barometric pressure, P_{H_2O} = vapor pressure of H_2O at temp.

T = absolute temp. (°A)

IV. Calculations

A. From titration of NaF pellets:

$$\text{Liters HF (at STP)} = \frac{(22.41)\,(\text{ml. NaOH x N} - \text{ml. H}_2SO_4 \text{ x N})}{1000} \tag{1}$$

B. From titration of NaOH at exhaust:

$$\text{Liters Cl}_2 \text{ (at STP)} = \frac{(22.06)}{(2000)} \text{ (ml. Na}_2S_2O_3)\,(N \text{ Na}_2S_2O_3)\,(50) \tag{2}$$

C. From bulb analysis:

$$\text{Ml. } O_2 \text{ (at STP)} = \text{(ml. abs. by pyrogallol)} \frac{(P-P_{H_2O})\,(273)}{(760)\quad(T)} \tag{3}$$

$$\text{Ml. G-74 (at STP)} = \left[(\text{Orsat sample} - \text{ml. abs. by pyrogallol})\right]$$

$$\left[\frac{(P-P_{H_2O})}{(760)} \quad \frac{(273)}{(T)}\right] \tag{4}$$

$$\text{Ml. Cl}_2 \text{ (at STP)} = \left[\text{Vol. bulb} - \frac{P - P_{H_2O}}{(P)} (\text{Orsat sample})\right] \frac{(P)}{(760)} \frac{(273)}{(T)} \tag{5}$$

$$\text{Total vol. (STP)} = \text{ml. O}_2 \text{ (STP)} + \text{ml. G-74 (STP)} + \text{ml. Cl}_2 \text{ (STP)} \tag{6}$$

$$\text{bulb \% O}_2 \frac{(\text{ml. O}_2)\,(100)}{\text{total volume}} \tag{7}$$

$$\text{bulb \% G-74} = \frac{(\text{ml. G-74})\,(100)}{\text{total volume}} \tag{8}$$

$$\text{bulb \% Cl}_2 = \frac{(\text{ml. Cl}_2)\,(100)}{\text{total volume}} \tag{9}$$

D. The final analysis is calculated as follows:

$$\text{Total liters Cl}_2 = \text{Vol. Cl}_2 \text{ from eq. 2} + \frac{\text{ml. Cl}_2 \text{ from eq. 5}}{1000} \tag{10}$$

$$\text{Total liters O}_2 = (\text{bulb \% O}_2) \frac{(\text{total liters Cl}_2)}{(\text{bulb \% Cl}_2)} \tag{11}$$

$$\text{Total liters G-74} = (\text{bulb \% G-74}) \frac{(\text{total liters Cl}_2)}{\text{bulb \% Cl}_2} \tag{12}$$

$$\text{Final volume} = \text{total liters O}_2 + \text{total liters G-74} + \text{total}$$

$$\text{liters HF} + \text{total liters Cl}_2 \tag{13}$$

$$\text{Final \% C-216} = \frac{(\text{total liters Cl}_2)\,(100)}{\text{Final volume}} \tag{14}$$

$$\text{Final \% HF} = \frac{(\text{total liters HF})\,(100)}{\text{Final volume}} \tag{15}$$

$$\text{Final \% O}_2 = \frac{(\text{total liters O}_2)\,(100)}{\text{Final volume}} \tag{16}$$

$$\text{Final \% G-74} = \frac{(\text{total liters G-74})\,(100)}{\text{Final volume}}$$

Sample calculation:

A. 50 ml. of 0.0987 N NaOH were added to the pellets in the mortar. 10.52 ml. of 0.2993 N H_2SO_4 were required for back titration.

By equation (1)

$$\text{Liters HF (at STP)} = \frac{(22.41)\;[(50 \times 0.0937) - (10.52 \times 0.2993)]}{1000}$$

Liters HF (at STP) = 0.040 l.

B. The solution in flask 10 was diluted to 500 ml. and 10 ml. of this solution was taken for titration. The titration required 44 ml. of 0.1030 N $Na_2S_2O_3$.

By equation (2)

$$\text{Liters } Cl_2 \text{ at STP} = \frac{(22.06)}{(2000)}(44)(0.1030)(50)$$

Liters Cl_2 at STP = 2.5 liters.

C. From bulb analysis

P = 750 mm. Hg, T = 300° A. VP H_2O = 26.74 mm. (at 300° A.)

302 ml. = volume of bulb

4.8 ml. = volume of gas after NaOH (orsat sample)

This sample was diluted to 30 ml. with G-74 (dilute volume)

The volume of the gas after the pyrogallol was 28.8.

30 - 28.8 = 1.2 ml. = ml. O_2

From equation (3)

$$\text{Ml. } O_2 \text{ (at STP)} = (1.2)\frac{(750 - 26.74)}{(760)}\frac{(273)}{(300)}$$

Ml. O_2 (at STP) = 1.04 ml.

From equation (4)

4.8 - 1.2 = 3.6 ml. = ml. G-74

$$\text{Ml. G-74 (at STP)} = (3.6)\frac{(750 - 26.74)}{(760)}\frac{(273)}{(300)}$$

Ml. G-74 (at STP) = 3.1 ml.

From equation (5)

$$Ml.\ Cl_2\ (at\ STP) = \left[302 - \frac{(750 - 26.74)}{(750)}\right](4.8)\quad \frac{(750)}{(760)}\frac{(273)}{(300)}$$

Ml. Cl_2 = 267 ml.

From equation (6)

Total volume (STP) = 1.04 / 3.1 / 267 = 271.14 ml.

From equation (7)

Bulb % O_2 = $\frac{(1.04 \times 100)}{271.14}$ = 0.4%

From equation (8)

bulb % G-74 = $\frac{(3.1)(100)}{271.14}$ = 1.1%

From equation (9)

Bulb % Cl_2 = $\frac{(267)(100)}{271.14}$ = 98.5%

D. Final analysis

From equation (10)

Total liters Cl_2 = 2.5 / $\frac{267}{1000}$ = 2.8 liters

From equation (11)

Total liters O_2 = (0.4) $\frac{(2.8)}{(98.5)}$ = 0.01

From equation (12)

Total liters G-74 = (1.1) $\frac{(2.8)}{(98.5)}$ = 0.03

From equation (13)

Final volume = 0.01 / 0.03 / 0.04 / 2.8 = 2.88

From equation (14)

Final % C-216 = $\frac{(2.8)(100)}{2.88}$ = 97.3%

From equation (15)

Final % HF = $\dfrac{(0.04)\ (100)}{2.88}$ = 1.4%

From equation (16)

Final % O_2 = $\dfrac{(0.01)\ (100)}{2.88}$ = 0.3%

From equation (17)

Final % C-74 = $\dfrac{(0.03)\ (100)}{2.88}$ = 1.0%

4.1-1

FIGURE 1
APPARATUS FOR C-216 ANALYSIS
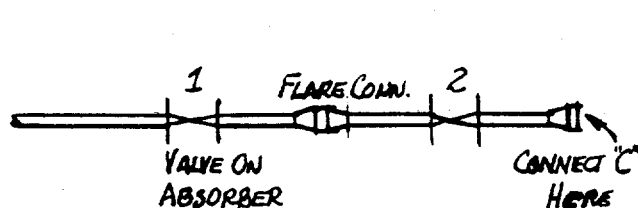
A. SAMPLING CONNECTION ON ABSORBER
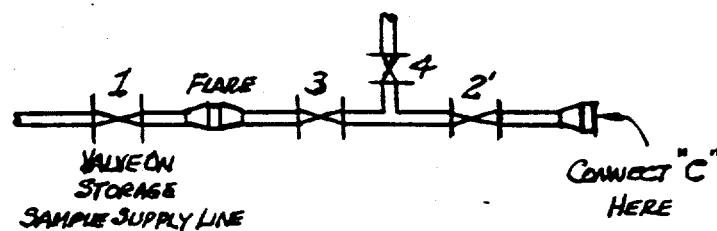
B. SAMPLING CONNECTION FOR STORAGE SAMPLE ANALYSIS
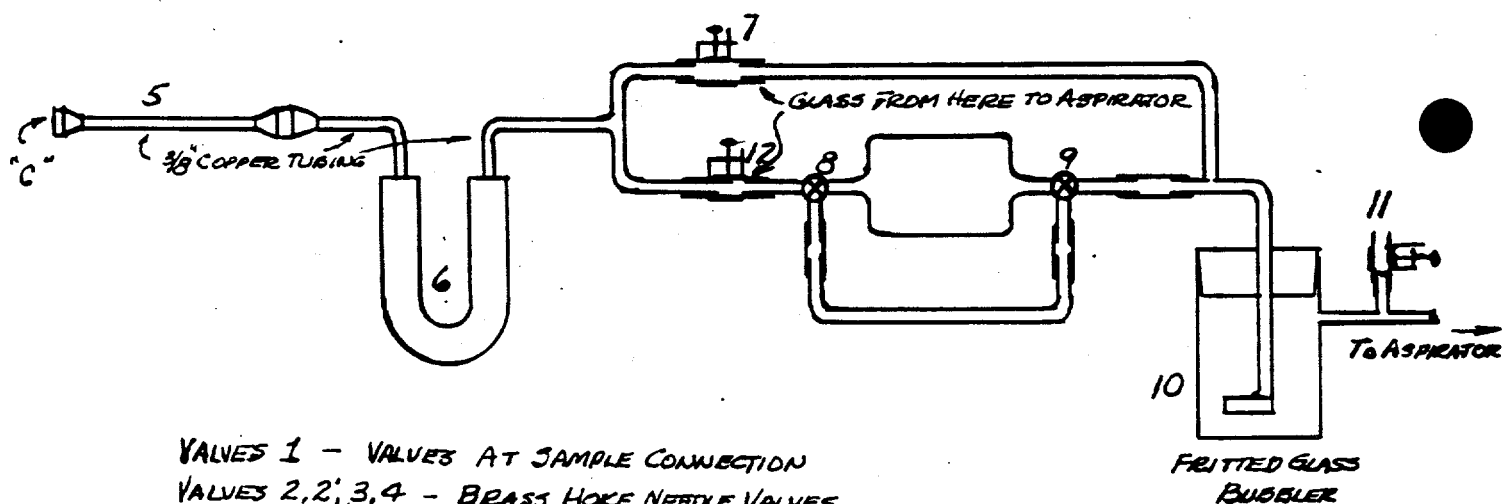
VALVES 1 — VALVES AT SAMPLE CONNECTION
VALVES 2, 2, 3, 4 — BRASS HOKE NEEDLE VALVES
#5 — 3/8" COPPER TUBE FILLED WITH 10g. NaF
#6 — NICKEL TUBE FILLED WITH NaCl
#7, #11, #12 — HOFFMAN CLAMPS FOR RUBBER TUBING CONNECTORS
#8, #9 — 3-WAY STOPCOCKS ON 300 ml. SAMPLING BULB FOR DETERMINING OXYGEN
#10 — 250 ml. 5% NaOH IN FRITTED GLASS BUBBLER

DETERMINATION OF C-216 IN CONDITIONING GASES

This is a method for the determination of C-216 in G-74 by the liberation of iodine by C-216, from KI solution. The iodine is titrated with standard sodium thiosulfate using starch as an indicator. This method can also be used when there is C-616 and HF in the gas.

I. Apparatus

A. Sample bulb - One liter sample bulbs with adapters as shown in Figure 1 are required.

B. Ten ml. automatic burette with reservoir.

C. KI dispenser - A 200 ml. round bottom flask with a tube fitted with 18/9 female spherical joint on the bottom. (See Figure 1).

D. Sample buggy - the sample buggy shown in Figure 2 is used to take samples.

SOME DO'S AND DON'TS ON THE CARE OF THE BUGGY

1. Don't move a buggy if the lines are evacuated.

2. Do open the valves to admit air into the manometer before moving.

3. Don't fail to take a leak rate on all connections before sampling.

4. Don't use Apiezon-Q to stop a leak; however, it may be used to find a leak.

5. Do your best to stop leaks by tightening the couplings.

6. Don't remove a stuck pump and install a new one.

   NOTE: A buggy with a stuck pump shows that the trap is exhausted.

7. Do return buggies with stuck pumps to Works Laboratory Field Office, 303-10, for repairs.

8. Use two wrenches for tightening flare fittings.

   NOTE: Use of only one wrench may twist tubing or break the

   buggy manifold.

9. Don't open the manometer to a vacuum quickly, as this may pull

mercury into the lines.

10. Don't bend the copper tubing leading from the buggy to the

sampling point. Disconnect it completely when moving a buggy.

II. Solutions Required

   A. 0.2 N Sodium Thiosulfate - Dissolve 50 grams of analytical re-

agent grade $Na_2S_2O_3.5H_2O$ in distilled water. Add 2 grams NaOH and

dilute to 1 liter with distilled water.

   Standardization: Prepare a 0.100 N potassium dichromate solution

as follows: Dry about 10 grams of finely ground analytical reagent

grade $K_2Cr_2O_7$ in an oven at 110° C. for at least two hours. Weigh out

4.903 grams of the dried salt, dissolve in distilled water and dilute

in a volumetric flask to one liter.

   Dissolve 2-3 grams of KI in 200 ml. of distilled water and add 10

ml. of 1:1 HCl. Measure accurately, from a burette into a glass

stoppered flask containing the KI solution, 60-80 ml. of the 0.1 N

potassium dichromate, and allow to stand for a period of 5-10 minutes.

Titrate with the $Na_2S_2O_3$ solution until the solution is light yellow.

Add 2-3 ml. of starch indicator and titrate to the disappearance of the

blue starch color. (A slight green color will remain).

Calculation:

$$N\ Na_2S_2O_3 = \frac{(ml.\ K_2Cr_2O_7)\ (0.100)}{ml.\ Na_2S_2O_3}$$

B. Ten per cent KI - Dissolve 100 grams of analytical reagent grade KI in 900 ml. of distilled water.

C. Starch Solution - Mix 5 grams of soluble starch thoroughly with a little distilled water. Pour the paste with constant stirring into 500 ml. of boiling water. Allow to cool and add 10 grams of KI.

D. Acetone.

E. MFI Grease.

III. Procedure

A. Testing buggy for leaks (this procedure should be carried out whenever buggy is used. As a rule, no leaks will be found and the procedure will not take but a few minutes).

WHEN OPERATING BUGGY AND GLASS BULBS ARE UNDER VACUUM, SAFETY GLASSES MUST BE WORN.

1. Close all valves.

2. Connect the buggy to sampling point and plug in pump cord on 110 volts A.C.

3. Start vacuum pump. Open valve E.

4. Open valve B slowly, taking care that no mercury is pulled into the line from the manometer. Allow system to pump until the pressure is less than 5 mm. absolute.

5. Close valve B and watch manometer for evidence of leaks.

   (a) If there is a leak, close valve E, and watch manometer for indications of a leak. Indications of a leak here

show that the connections to the manometer are not tight. Tighten carefully, if leak does not stop, get a new buggy and return the old buggy to Works Laboratory Field Office, 303-10, for repairs.

(b) If closing valve E stops the falling off of the manometer, check valves A, C, C^1, and D. Open valve E again and see if the leak was due to a valve which may have been opened slightly. If there is still a slight leak or if there was not any leak at the beginning, proceed with the following testing.

6. Open valves D and B and evacuate the purge bulb.

7. Close valve B and watch manometer for indication of leaks.

(a) If there was a leak indicated in (b) of step 5, and no indication of a leak at this point, then valve D leaks through the seat. Make a notation of this, if leak was very small (5 mm. per minute or less), the buggy can still be used. If there is still a leak, but it is much slower, indications are that valve D and the purge bulb are not leaking.

(b) If there was not a leak before and there are indications of a leak now, the bulb leaks and the buggy should be sent to Works Laboratory, Field Office, 303-10 for repairs.

(c) If there are not any leaks, proceed with Step 8.

8. Close valve D, open valves A and B, making sure that the valves on the line recorder manifold or other sampling point are closed.

9. Close valve B and watch manometer for leaks.

(a) If there was a leak in Step 5(b), and there is none now, valve A leaks through the seat. Make a notation and report the fact to the supervisor. The buggy can still be used.

(b) If there was a leak in Step 5 (b) and there is still about the same leak, proceed with Step 10. If the leak seems greater, tighten the flare fittings and check the valves on the sampling point. Proceed with Step 10.

10. Close valve A and attach bulbs to fittings above valves C and C^1. Make sure the stopcocks and the spherical joint are well greased with MFI grease.

11. Open valves C, C^1 and B, evacuating the short lines between valves C, C^1 and the stopcocks on the bulbs.

12. Close valve B and watch manometer for leaks.

(a) If there was a leak indicated in Step 5 (b) and no leak now, then either valve C or C^1 leaks through the seat. Close both valves and open the stopcock on the bulb over valve C. If there is a leak through the valve C, it will show on the manometer. If there is not a leak, open the stopcock on the bulb over valve C^1. If there is a leak through this valve, it will show on the manometer.

(b) If there was a leak indicated in Step 5 (b) and it continued whether valves C and C^1 were opened or closed, it can be assumed that the buggy manifold is at fault. If this is the case, take the buggy to Works Laboratory Field Office, 303-10, for repairs.

(c) If no leaks were found in all 12 steps, the buggy is ready to take a sample.

(d) If there was a leak in Step 9 (c), isolate it in the following manner:

Disconnect the copper tube from the sampling manifold at the manifold and plug up the end of the copper tube with a rubber stopper. Open valves A and B, close valves C, C^1 and D and evacuate the line. Close valve B and watch manometer for a leak. If there is a leak, tighten the flare fitting connecting the copper line to the buggy. If this does not stop the leak, close valve A, disconnect the copper line and check the flare for cracks. If there is not a leak, connect the line back to the sampling manifold after first looking for a defective flare at this joint. Then evacuate the line, close valve B and watch manometer. If there is still a leak, use some Apiezon-Q over the flare fittings. If this stops the leak, tighten the flare connections and remove the Apiezon-Q. If this does not

remove the leak, the valve on the sampling manifold is at fault. Notify the supervisor of this fact. If the system is now tight, the sample may be taken.

B. Cleaning of bulbs

1. Rinse the bulb thoroughly with distilled water.

2. Rinse the bulb with acetone and wash MFI grease off the stopcock and the ground joint with acetone.

3. Blow the bulb completely free of acetone liquid and vapor with dry G-74.

4. Regrease both the stopcock and ground glass joint with MFI.

C. Procedure for Taking C-216 Sample

1. Open all valves* except the valve on the sampling manifold.
   NOTE: When set up at a line recorder station, open the valve on the sampling manifold, but be sure the valve on the loop is closed. Check with line recorder operator.

2. Let system come to equilibrium. This requires 5-10 minutes.

3. Read the manometer (both sides if it is a U-tube) record the pressure (if the manometer is a U-tube, record the difference). This is the starting pressure.

4. Close valves C, C^1, and D. Close valve B, open valve D, and have operator open sampling valve. This purges the line into the metal bulb.

5. When pressure reaches equilibrium, about 1-2 minutes, close valve D and open valve C or C^1 and allow gas to fill bulb.

---

* If only one bulb is being used valve C or C^1, at whichever point the bulb is attached, is opened while the other valve remains closed.

6. Close valve A and read the pressure (both sides if using a U-tube manometer).

7. The difference between this pressure and the starting pressure is the pressure of the sample. Important - the sample pressure is to be recorded in millimeters of mercury.

8. Close stopcock and have operator close the sampling valve.

9. Open valves A and B, and D, evacuate the lines, then close valve C or C[1] (whichever one the sampling bulb was attached to).

10. Remove the bulb. Record the time, temperature, pressure and volume of the bulb.

11. If there was a blue flash or flame in the bulb during Step 5, evacuate and start over.

D. The Analysis of C-216

1. Fit the male spherical joint on the bulb into the female joint of the KI dispenser.

2. Pour about 50 to 100 ml. of 10 per cent KI solution into dispenser.

3. Open stopcock on dispenser if it has one. Then open stopcock on bulb and allow all of the KI solution to flow into the bulb. Close stopcock on bulb as soon as air begins to hiss.

4. Remove bulb from the KI dispenser and shake bulb well, about 2-4 minutes, or until the white fumes in the bulb disappear.

5. Place bulb in cork ring with stopcock up. Open stopcock and wash inside of adapter with distilled water.

6. Fill burette with 0.2 N sodium thiosulphate solution.

7. Remove adapter from bulb and titrate the liberated iodine with thiosulfate to a light yellow, then add starch indicator and continue this titration to the point where the solution turns from blue to colorless.

8. Record the volume of thiosulphate used.

IV. Calculations

To calculate the percentage of C-216.

$$\%C\text{-}216 = \frac{(\text{ml. } Na_2S_2O_3)\ (N\ Na_2S_2O_3)\ \left(\frac{22,400}{2000}\right)\ (100)}{(\text{Volume of bulb})\ \left(\frac{\text{Pressure in mm.}}{760}\right)\ \left(\frac{273}{\text{Absolute temperature}}\right)}$$

Combing the constants in the above equation into one factor (F)

$$F = \frac{(N\ Na_2S_2O_3)\ (22,400)\ (100)\ (760)}{(273)\ (2000)}$$

Therefore,

$$\%\ 216 = \frac{(F)\ (\text{ml. } Na_2S_2O_3)\ (\text{absolute temperature})}{(\text{Volume of bulb})\ (\text{Pressure in mm.})}$$

Sample calculation:

Temperature equals 27° C. = 300° A

Volume of bulb = 1020 ml.

Pressure = 142 mm.

Ml. thiosulfate used = 9.15

The normality of the thiosulfate is 0.1982

Substituting this value into the above equation:

$$F = \frac{(0.1982)\ (22,400)\ (100)\ (760)}{(273)\ (2000)} = 618$$

$$\%\ C\text{-}216 = \frac{(618)\ (9.15)\ (300)}{(1020)\ (142)}$$

C-216 = 11.7 per cent.
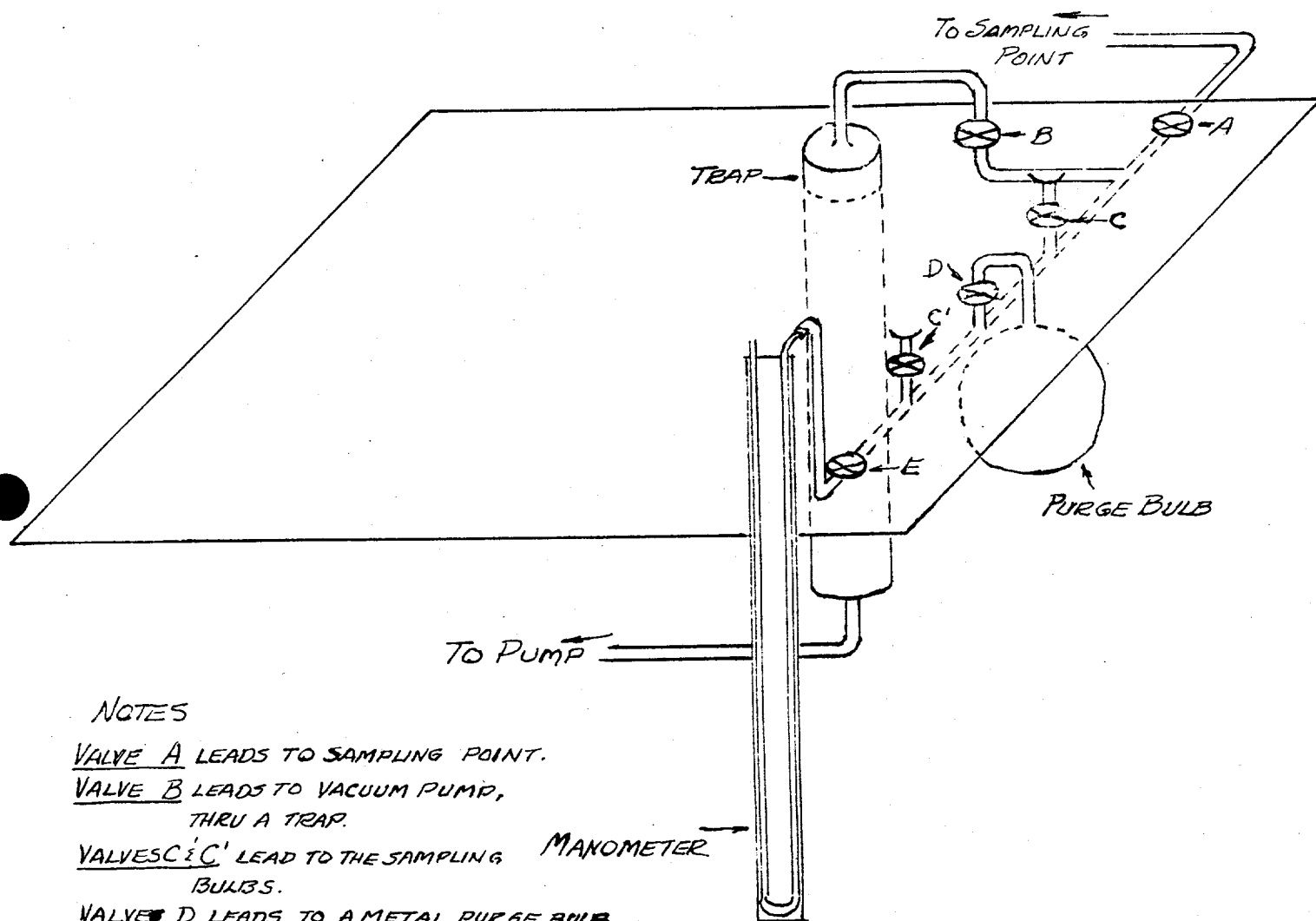
TAPERED STOPPER
24/40 FEMALE

4MM. STRAIGHT
BORE STOPCOCK

200 ML.
BULB

BALL JOINT
18/9 FEMALE

TAPERED STOPPER
24/40 MALE

B. KI DISPENSER

BALL JOINT
18/9 MALE

A. ADAPTER FOR
SAMPLING BULB

I - LITER BULB
ROUND BOTTOM

C. SAMPLING BULB

FIGURE I

FIGURE 2

WORKS LABORATORY SAMPLING BUGGY

NOTES

VALVE A LEADS TO SAMPLING POINT.

VALVE B LEADS TO VACUUM PUMP, THRU A TRAP.

VALVES C & C' LEAD TO THE SAMPLING BULBS.

VALVE D LEADS TO A METAL PURGE BULB.

VALVE E LEADS TO THE MANOMETER

HRB 9-17-?

DETERMINATION OF HF IN C-216 AND G-74 MIXTURES

This method is for the determination of HF in C-216 and G-74 mixtures. The gas is reacted with water and the resulting solution titrated with standard alkali. It is to be used in conjunction with the analysis for C-216.

I. Apparatus

Same as used in sampling and analyses of C-216. Refer to "Determination of C-216 in Conditioning Gases."

II. Reagents

A. 0.1 N NaOH

Weigh 4.5 grams of analytical reagent grade NaOH (pellet) on a trip balance, dissolve in 100 ml. of distilled water, and dilute to one liter.

Standardization: Dry 10 grams of primary standard potassium acid phthalate in an oven for at least two hours. Weigh accurately three portions of approximately 0.9 gram potassium acid phthalate on an analytical balance. Treat each portion in the following manner: Dissolve the potassium acid phthalate in 50 ml. of CO_2-free water in a 250 ml. Erlenmeyer flask. Add 2 drops of phenolphthalein indicator and titrate to a faint pink color with 0.1 N NaOH.

Calculation:

$$N \text{ NaOH} = \frac{\text{grams potassium acid phthalate}}{(\text{ml. NaOH}) \ (0.2041)}$$

B. 0.1 N HCl

Add 8.5 ml. concentrated HCl to 500 ml. distilled water and dilute to one liter. Standardize against the standard 0.1 N NaOH solution using phenolphthalein as an indicator.

-2-

Calculation:

$$N\ HCl\ =\ \frac{(ml.\ NaOH)\ (N\ NaOH)}{(ml.\ HCl)}$$

C. Acetone

D. MFI grease

III. Procedure

The sample is taken immediately after a C-216 sample; so it is assumed the buggy is leak tight. In other instances, however, test for leaks in the same way as outlined in procedure for C-216 analysis.

A. Cleaning of Bulbs

1. Rinse bulb thoroughly with distilled water.

2. Rinse bulb with acetone and remove MFI grease from stop-cocks and glass joints with acetone.

3. Blow bulb completely free of acetone liquid and vapor with dry G-74.

4. Regrease both the stopcock and ground glass joints with MFI.

B. Taking of Sample

1. Follow sampling procedure outlined in C-216 analysis and take enough sample to change the pressure 100-125 mm.

2. Remove bulb, recording temperature, pressure of sample, and volume of bulb.

3. Pour about 125 ml. distilled water into KI dispenser.

4. Allow about 100 ml. of water to run into bulb taking care that no air gets into the bulb.

5. Shake bulb for about 2 minutes, until the cloud disappears completely.

6. Add 25 ml. 0.1 N NaOH from a pipet to the dispenser and then into the bulb. It may be necessary to add another 25 ml. to make the solution alkaline.

7. Rinse the dispenser several times with small portions of distilled water, until a drop of phenolphthalein remains colorless when added to the water, and add to bulb.

8. Shake bulb vigorously for five minutes.

9. Titrate solution with 0.1 N HCl using phenolphthalein as indicator.

IV. Calculations

C-216 per cent previously determined on a separate sample.

$$\text{Total \% HF} = \frac{(N\ NaOH)\ (ml.\ NaOH - ml.\ HCl)\ (22.4)}{1000\ (vol.\ of\ bulb\ in\ L)}\ \frac{(760)}{Pres.}\ \frac{(T.\ ^{\circ}A)}{(273)} \times 100$$

(Original HF and that formed by reaction of C-216 and water).

% HF = Total % HF - 2(C-216 %) (Assuming all F from C-216 is converted to HF)

FLUORIDE DETERMINATION IN SPENT CARBON AND ACTIVATED ALUMINA

Method:

Fluoride in the samples is converted to a soluble form by alkaline fusion. The fluoride is separated as hydrofluoric acid by distillation from an acid solution. The hydrofluoric acid is received in dilute alkali. Buffer is added and the solution is titrated with standard thorium nitrate to a pink end point using sodium alizarin sulfate indicator.

Apparatus and Reagents:

1. Sulfur-free powdered sodium peroxide.

2. Powdered c.p. potassium perchlorate.

3. Powdered c.p. benzoic acid.

4. Sodium carbonate, c.p. anhydrous.

5. Sulfuric acid, concentrated.

6. Sodium alizarin sulfonate solution - 1 per cent.

7. Hydrochloric acid solution, approximately 0.05 N.

8. Sodium hydroxide solution, approximately 1 per cent.

9. Monochloracetic acid buffer solution - Dissolve 38 g. of mono-chloracetic acid in 100 ml. of distilled water. Neutralize 50 ml. of this solution with sodium hydroxide; combine with the remainder of the solution; and make up to 200 ml. volume with distilled water.

10. Thorium nitrate solution, approximately 0.1 N.

11. Standard sodium fluoride - Prepared from recrystallized sodium fluoride.

12. The combustion bomb - The Parr coal sulfur bomb, or its equivalent should be used for the fusion of spent carbon. A nickel crucible should be used for the fusion of activated alumina.

Procedure:

A. Preparation of Spent Carbon Samples:

1. Weigh 1 g. of potassium perchlorate and 0.3 g. of benzoic acid into a dry sulfur bomb. Add 0.5 g. of the sample and mix thoroughly with a glass rod.

2. Add approximately 15 g. of sodium peroxide, close the bomb, and mix thoroughly by shaking.

3. Remove the bomb cover, and place about 0.5 g. of potassium perchlorate, and about 0.1 g. of benzoic acid on top of the charge so that the ignition wire can come in contact with it.

4. Fasten the cover securely to the bomb and ignite the charge by electric ignition. Allow a few minutes for complete combustion to take place after ignition, then cool the bomb under tap water.

5. Remove the cover from the bomb; place the bomb on its side in a 400 ml. beaker and wash the cover with a fine jet of hot distilled water.

6. Place a watch glass over the beaker, and cautiously add about 100 ml. of hot distilled water. After the contents of the bomb have dissolved, remove and rinse the bomb carefully with the distilled water.

7. Filter through Whatman No. 41 filter paper and wash several times with distilled water.

B. Preparation of Activated Alumina Samples:

1. Place 2 g. of the powdered sample in a nickel crucible, and add about five or six times as much sodium carbonate. Mix thoroughly with a glass rod, and heat over a gas flame until the mixture is molten.

2. Remove the crucible and its contents from the flame and allow to cool thoroughly. Transfer the fused mixture to a 400 ml. beaker using hot distilled water. (Although most of the alumina is not affected by the fusion, any fluoride which may be present is converted to sodium fluoride which is dissolved in the hot water.)

3. Filter through qualitative filter paper and wash the insoluble residue several times with distilled water. If the volume of the filtrate is over 150 ml. evaporate it to 150 ml. on a hot plate.

C. Distillation of Fluoride:

1. Neutralize the filtrate containing the fluoride with concentrated sulfuric acid and add about 10 ml. in excess. Transfer this solution to the distillation flask which is connected to a condenser through a suitable splash trap and heat the flask with a gas flame.

2. Collect the distillate in a 400 ml. beaker. During the distillation keep the outlet of the condenser beneath the level of the distillate in the receiver.

3. When the temperature has reached 125° C., connect the distillation flask to a source of steam and complete the operation as a steam distillation.

4. Collect about 200 ml. of the distillate between the temperatures of 125° C. - 140° C., keeping the distillate slightly alkaline to phenolphthalein by adding 1 per cent sodium hydroxide solution to the receiver as needed.

   Caution: Do not allow the distillation temperature to exceed 150° C. because interfering substances may be distilled above this temperature.

-4-

D. Titration:

1. Transfer the distillate to a 500 ml. volumetric flask and make it up to volume with distilled water.

2. Pipette a suitable aliquot into a 100 ml. Nessler tube and dilute to approximately 90 ml. with distilled water. (From the quantity of 1 per cent sodium hydroxide needed to keep the distillate slightly alkaline, one may estimate the appropriate aliquot to be taken for titration).

3. To the aliquot add 2 drops of 1 per cent sodium alizarin sulfonate. This will impart a pink color to the solution.

4. Add 0.05 N hydrochloric acid dropwise to the sample until the solution becomes pale green, then add 2 drops in excess. Add 2 drops of monochloracetic acid buffer solution.

5. Titrate the buffered solution with standard thorium nitrate solution until the first pink color appears. Record the volume of thorium nitrate required.

6. Determine the fluorine equivalent of the thorium nitrate solution by titrating a known amount of standard sodium fluoride solution made from recrystallized sodium fluoride against the thorium nitrate solution using sodium alizarin sulfonate as indicator. The same procedure is used for this titration as in Steps 1 to 5 above.

Calculations:

1. $T \times A = mg.$ fluorine in aliquot

   $T =$ ml. standard thorium nitrate required to titrate sample aliquot

   $A =$ fluorine equivalent of standard thorium nitrate solution (determined in Step 6, Part D above) expressed as mg. of fluorine equivalent to one ml. of standard thorium nitrate solution.

2. $\dfrac{\text{Mg. fluorine in aliquot} \times \dfrac{\text{Total volume of sample solution}}{\text{Volume of aliquot}}}{\text{Sample weight (mg.)}} = \begin{array}{l}\text{\% fluorine}\\ \text{in sample}\end{array}$

3. $\dfrac{\text{Weight of sample}}{\text{Weight of mixture}} \times \text{\% fluorine in sample} = \text{\% fluorine in mixture}$

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ANALYSIS OF FURNACE GASES

By use of special gas bulbs we control and determine concentration of C-216, O_2 and HF used in conditioning of units. Also, we detect presence of C-216 in special tests.

Apparatus:

    Gas sampling bulb

    Clamp

    Safety sample apparatus

    Hot porosity apparatus

    Final porosity apparatus

Reagents:

    10% KI

    0.1 N $Na_2S_2O_3$

    Starch indicator solution

    Bromthymol blue indicator solution

    Approximately 0.01 N NaOH

    Approximately 0.01 N HCl

    Phenolphthalein

Procedure:

    C-216 analysis (KI method)

Sampling Schedule:

    Sample #1 - 10 minutes after initial addition of C-216.

    Sample #2 - 20 minutes after C-216 addition completed.

    The concentration of C-216 must be 10% or more; if not, area must add 0.2# C-216 for every 1% C-216 is low.

A check sample should be taken after C-216 addition.

Samples are to be taken every 2 hours after second sample (regardless of how many check samples on C-216 addition are required) until final sample.

The concentration of C-216 must be above 5%; if not, it must be brought to 6% with C-216 similar to addition procedure in sample #2.

Sample #3 — Final sample when notified by Area. Analysis for C-216, O_2 and HF required.

Sampling Procedure:

1. Check bulb and use if clean and dry. Cleaning is accomplished by washing with TCE, H_2O, CSR, H_2O, cleaning solution, H_2O, in that order; rinsed in alcohol and acetone, and dried on vacuum set-up.

2. Check and see if Stokes pump is on; if not, notify operator.

3. Attach bulb with clamp to sampling connections.

4. Open Stokes pump valve (Vacuum system) to maximum vacuum. Attach rubber hose to bottom of bulb. Check vacuum.

5. Open bottom and top stopcocks and evacuate bulb for 1 minute.

6. After a minute close bottom stopcock and open C-216 main sampling valve. Collect sample.

7. Close main sampling valve and open bottom stopcock. Evacuate bulb as in step 5. This is to purge line completely.

8. After bulb is evacuated close bottom stopcock and open C-216 main sampling valve and collect sample. Turn bottom stopcock one full turn and close — after 15 seconds close top stopcock, and then main C-216 sampling valve. Read pressure from furnace panel.

   Note: (Subtract 0.4 lbs. from furnace pressure and record answer as final pressure.)

Place hose on upper side arm of bulb and evacuate sample line.

This is to eliminate any C-216 that is present. Shut Stokes pump valve.

9. Remove bulb from connection, first removing rubber hose.

Note: (Place rubber nipple on glass sampling joint.)

Analysis of C-216

Attach rubber tube from KI reservoir to bottom of bulb. Purge side arm

of bulb. Admit KI solution to bulb. Close bottom stopcock and shake bulb

until dense white fog in bulb disappears. Wash sample into beaker with KI

solution. Flush bulb with KI solution until solution in bulb is colorless.

Note: (On final sample leave small amount KI in bulb to act as

seal. Prevent air from entering bulb.)

Titrate sample with 0.01 N (approx.) $Na_2S_2O_3$ solution (using starch

solution as indicator) until solution turns from blue to colorless. Record

titration data in proper place on work sheet. Save solution for HF determina-

tion.

Note: (Fill buret to zero mark after recording titration data; also

check zero at beginning of titration.)

Calculation of C-216

1. (ml. $Na_2S_2O_3$) (normality $Na_2S_2O_3$)(11.2) = Vol. C-216 at standard
    conditions.

2. (Bulb vol.) $\left(\dfrac{\text{bulb pressure}}{14.7}\right)\left(\dfrac{273}{298}\right)$ = Vol. sample at standard conditions.

3. $\dfrac{(\text{ml. } Na_2S_2O_3)(\text{normality } Na_2S_2O_3)(11.2)(14.7)(298)}{(\text{bulb volume})(\text{bulb pressure})(273)}$ = %C-216

4. $\dfrac{(\text{ml. } Na_2S_2O_3)(\text{factor})}{(\text{bulb vol.})(\text{furnace pressure})}$ = %C-216

Note: (#4 is a simplification of 1, 2 and 3.)

-4-

Analysis of HF

Add 10 ml. of 0.05 N NaOH solution, (excess wanted is indicated by blue color remaining permanent for 15 minutes on using bromthymol blue as indicator) to solution from C-216 analysis. Back-titrate with 0.05 N HCl to end-point: blue changes to pale green.

Calculation of HF:

1. (ml. NaOH - ml. HCl)(N)(22.4) = vol. HF at standard conditions.

2. (Bulb vol.) $\dfrac{(\text{furnace press.})(273)}{(14.7)(298)}$ = vol. sample.

3. $\dfrac{(\text{Vol. HF})(100)}{\text{Vol. sample}}$ = %HF

4. $\dfrac{(\text{ml. NaOH - ml. HCl})(\text{factor})}{(\text{Bulb capacity})(\text{bulb pressure})}$ = %HF

   Note: (#4 is a simplification of 1, 2 and 3.)

Analysis of O$_2$

Attach sampling bulb saved from C-216 analysis to three-way stopcock on O$_2$ gas analysis apparatus. Force gas in bulb into apparatus. Measure volume of gas in gas buret. Record data. Absorb O$_2$ from gas by passing into pyrogallol solution and measure volume of residual gas. When volume of residual gas becomes constant record data.

Calculation of O$_2$:

V_1 = Original volume of gas in buret.

V_2 = Volume of gas after O$_2$ is absorbed, (constant volume).

1. $V_1 - V_2$ = Volume of O$_2$

2. (Bulb vol.) $\dfrac{(\text{furnace pressure})}{(14.7)}$ = Volume of sample

4.5

3. $\dfrac{(\text{vol. } O_2)(100)}{(\text{vol. sample})} = \% \ O_2$

4. $\dfrac{(V_1 - V_2)(14.5)}{(\text{Bulb vol.})(\text{furnace pressure})} = \% \ O_2$

   Note: (#4 is a simplification of 1, 2 and 3.)

WEIGHT PROCEDURE FOR DETERMINATION OF HF IN FURNACE GASES

1. Check bulb and use if clean and dry. Cleaning and drying is done by washing with TCE, water, cleaning solution, water (in that order) rinsing in alcohol and acetone, and drying on vacuum set-up. Use MFI grease instead of C-2144 for stopcocks.

2. Apply vacuum to upper side-arm to remove any loose MFI. Evacuate with small vacuum pump for about 5 minutes, weigh bulb to 4 significant figures.

3. Clamp bulb on male joint with top and bottom stopcock closed. Open vacuum valve and attach tubing to upper side-arm; with upper stopcock still closed open main sampling valve (C-216 main valve). Purge through side-arm and then turn stopcock around to let sample (C-216) into bulb. Shut off vacuum valve and take pressure reading. This should be sufficient time for pressure of gas in furnace and bulb to be equalized. Close C-216 valve and purge line through side-arm and remove bulb.

Take bulb with sample in it up to main laboratory and re-weigh. Record differences in weight and run regular titration for C-216, HF and O_2.

Calculation for HF:

$$\frac{[(ml.\ NaOH)(Normality\ NaOH) - (ml.\ HCl)(Normality\ HCl)](0.020)(100)}{Weight\ of\ Gas} = \%HF\ by\ weight$$

$$\frac{(ml.\ Na_2S_2O_3)(Normality\ Na_2S_2O_3)(0.019)\ \ (100)}{Weight\ of\ Gas} = \%C\text{-}216\ by\ weight.$$

$$100 - (\%HF\ by\ weight + \%C\text{-}216\ by\ weight) = \%G\text{-}74\ by\ weight.$$

$$\frac{\left(\frac{\%HF}{20}\right)}{\frac{\%HF}{20} + \frac{\%C\text{-}216}{38} + \frac{\%G\text{-}74}{28}} = \%HF\ by\ volume$$

-1-

FLUORIDE DETERMINATION

Solutions

1. Thorium Nitrate

    Make up a solution of correct normality for titrating the amount of

    fluoride present and standardize with NaF.

2. Alizarin - Red-S Indicator

    Use 0.25 g. Sodium Alizarin Sulfonate per liter.

3. Reference Color Standard

    Two solutions are used and a new reference can be made at any time

    when necessary.

    Cobalt Nitrate (Hexahydrate)

    10.0 g. per liter

    Potassium Chromate (substituted for Tetrahydrate Sodium Chromate)

    0.109 g. per liter (Anhydrous was used).

    Color Standard

    10 ml. cobalt solution

    10 ml. chromate solution

    30 ml. water

4. Chloroacetic Acid Buffer Solution

    4 M Monocholoracetic acid solution.

    5 N Sodium Hydroxide.

    Neutralize 10 ml. 4 M monochloroacetic acid with 5 N NaOH

    (phenolphthalein indicator). Then add 10 ml. 4 M monochloroacetic

    acid and dilute to 40 ml.

    Make up fresh every two weeks. pH = 2.8

5. Nitric Acid

Make up solution using 1 part HNO_3 and 20 parts water.

Solids

Sample Size and Preparation:

Weigh a half-gram sample, place in a 500 ml. standard distilling flask which contains 100 ml. water and 30-35 ml. sulfuric acid. Connect a water-cooled condenser and insert a two-hole rubber stopper, which holds the thermometer and a thistle tube or dropping funnel so that additional water may be added. The distillate is received in an open beaker of distilled water. The thermometer and thistle tube must extend well below the surface of the liquid. If a thistle tube is used a connection must be made to allow for the dropwise addition of water. The condenser must extend below the surface of water in receiver.

In the distilling flask place a large amount of finely broken soft glass to act as boiling stones and provide a source of silica. If a large amount of fluoride is present more glass should be used.

Distillation

Apply heat gradually until the temperature rises to 145°C. collecting the distillate in the open beaker. Add water dropwise keeping the temperature between 136° and 145°C. Continue the addition of water until 300 ml. of water has been added, changing the receiver when necessary. After the final addition of water allow the temperature to rise to 150°C. Stop the distillation.

Titration of Distillate

Neutralize the distillate with 0.5 N NaOH and evaporate to 20 ml. if

there is a very small amount of fluoride present. If a larger amount is present make up to convenient volume in a volumetric flask and take an aliquot for titration.

To titrate with $Th(NO_3)_4$ use a 125 ml. Erlenmeyer flask for titration. Select aliquot size so that the sample will titrate between 5 and 45 ml. $Th(NO_3)_4$ if possible. Dilute the sample if necessary to make final titration volume approximately 50 ml. Add 15-20 drops Alizarin Red-S indicator. Neutralize sample to light pink with 1:20 HNO_3. Add 10 drops chloroacetic acid buffer solution. The solution is then a light yellow. Titrate with $Th(NO_3)_4$ to the reference color standard.

Calculations:

The blank is an indicator blank on water. It is not necessary to run this after each titration. Run only one on each new solution.

The factor is the grams F^- equivalent of the $Th(NO_3)_4$ solution.

$$g. \ F^- = (ml. - blank)(factor)$$

$$\% \ F^- = \frac{(g. \ F)(Vol. \ of \ dist.)(100)}{(Aliquot)(wt. \ of \ sample)}$$

Liquids

If a liquid sample is used the same procedure is followed except the sample is measured with a pipet. The sample should be within the range of 5-8 pH before the addition of acid for distillation. The size sample is selected according to the amount of fluoride present.

Calculations:

$$F^- \ g. = (titration - blank)(factor)$$

$$F^- \ g./L = \frac{(F^- \ g. \ )(Volume \ of \ distillate)(1000)}{(Aliquot) \quad (Ml. \ of \ sample)}$$

Apparatus Necessary for Distillation

1. Flask - Standard distillation, 500 ml.

2. Condenser - Water cooled, 18-24 inches long.

3. Receiver - Beaker, 250-400 ml.

4. Thermometer - Centigrade, 0-250°

5. Thistle Tube with glass tubing connected by rubber tubing and a
   pinch clamp to control addition. (Dropping funnel may be substi-
   tuted.)

100 ML CAPACITY FLASK
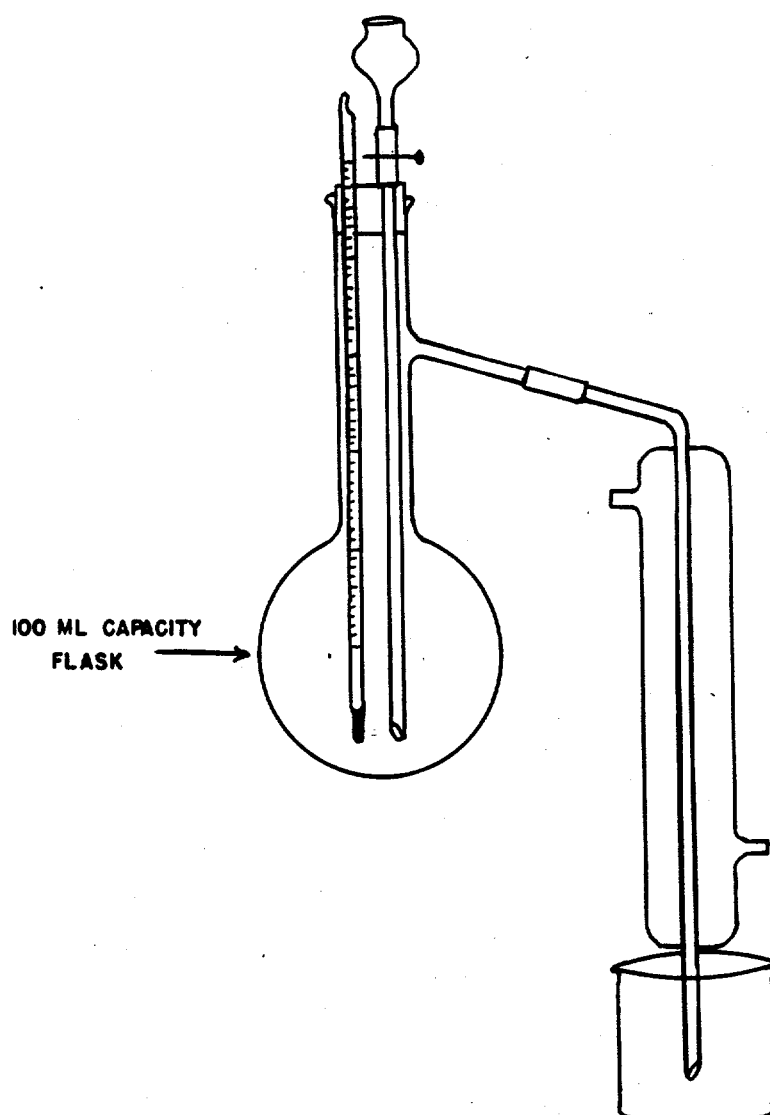
FLUORIDE DISTILLATION APPARATUS

FLUORIDES IN SETTLING TANK - DISPOSAL PLANT

Pipette a 1 ml. sample into a 125 ml. Erlenmeyer flask containing about 40 ml. of distilled water; mix. Add 15 drops Alizarin-S indicator. (The sample will turn a purple color). Add diluted nitric acid (1:20) until the color changes to a light pink. Add 10 drops buffer solution, (Monochloracetic Acid) to a straw yellow color. Titrate with Thorium Nitrate to end-point. (Value matching with reference standard).

Calculation:

Allow 0.15 for blank

Eq. wt. X titr. = F (mg/l.)

Take pH of titrated sample. Record.

Take turbidity using gray filter. Record reading.

Note: Solutions and indicators are made as per directions in "Distillation of Fluorides - Tentative Procedure".

OIL ANALYSIS

The following analyses are carried out using ASTM methods. Number after analysis refers to number of method in "A.S.T.M. Standards, 1942 Edition".

Viscosity (Saybolt)	D 88-38	
Viscosity (Kinematic)	D 445-42 T Method B	
Neutralization Number	D 663-42 T	
Flash Point (Open Cup)	D 92-33	1,2,3,4,6
Flash Point (Closed Cup)	D 93-42	
Fire Point	D 92-33	1,2,3,5,6
Pour Point	D 97-39	
Carbon Residue	D 189-41	
Ash	D 482-38 T	
Specific Gravity	D 287-39	
Precipitation Number	D 91-40	
Sedimentation Number	D 96-40	
Water	D 95-40	
Calorific Value	D 240-39	
Sulfur	D 219-39	

COAL ANALYSIS

The following analyses are carried out using ASTM methods.
Number after analysis refers to number of method in "A.S.T.M.
Standards, 1942 Edition".

Moisture	D 271-42	Sections 4,7
Ash	D 271-42	10,11
Volatile Matter	D 271-42	13,14
Sulfur	D 271-42	21
Calorific Value (Parr calorimeter)	D 271-42	40,41
Grindability	D 409-37 T	
Screen analysis	D 410-38	

GREASE ANALYSIS

The following analyses are carried out using ASTM methods.
Number after analysis refers to number of method in "A.S.T.M.
Standard, 1942 Edition".

Consistency	D 217-38 T	
Dropping Point	D 566-42	
Viscosity	D 88-38	
Ash	D 128-40	Section 5
Oil	D 128-40	15
Fatty acid (soap)	D 128-40	12
Fatty acid (free fat)	D 128-40	14
Inorganic residue	D 128-40	10
Asphalt or tarry matter	D 128-40	17
Free acid	D 128-40	20
Water	D 128-40	21
Melting Point	D 127-30	

REAGENTS REQUIRED FOR WATER ANALYSES

1. **Sulfuric acid (Approx. 4.3 N)** - Add 50 ml. concentrated reagent grade sulfuric acid to 366 ml. distilled water.

2. **Sulfuric acid (Approx. 2 N)** - Add 110 ml. concentrated reagent grade sulfuric acid slowly and with stirring to approximately 1 liter of distilled water in a 2000 ml. volumetric flask. Cool to about room temperature and make up to 2000 ml. mark with distilled water.

3. **Hydroquinone (2%)** - Dissolve 2.0 grams hydroquinone in 100 ml. 2 N H_2SO_4 (2).

4. **Carbonate-Sulfite Solution** - Dissolve 250 grams anhydrous sodium carbonate (or equivalent) in 1 liter distilled water. Dissolve 37.5 grams anhydrous sodium sulfite in 250 ml. distilled water. Add the sodium sulfite solution to the sodium carbonate solution.

5. **Molybdic Acid Solution** - Dissolve 10.0 grams finely ground ammonium molybdate in 200 ml. 2 N H_2SO_4 (2).

6. **Hydrochloric Acid (Approx. 3 N)** - Add 260 ml. concentrated HCl to 740 ml. distilled water.

7. **Hydroxylamine Hydrochloride (10%)** - Dissolve 10.0 grams NH_2OH. HCl in distilled water and dilute to 100 ml.

8. **Ortho-Phenanthroline (0.1%)** - To 1.000 gram ortho-phenanthroline (weighed on analytical balance) add about 500 ml. hot distilled water. When dissolved, cool to room temperature and dilute to exactly 1000 ml. in a 1000 ml. volumetric flask. Glassware must be scrupulously clean to avoid discoloration of the solution.

9. **Ammonium Acetate (30%)** - Dissolve 300 grams reagent in distilled water and dilute to 1 liter.

10. <u>Sodium Thiosulfate (.025 N)</u> - Dissolve about 6.2 grams $Na_2S_2O_3$.

    5 H_2O in distilled water and dilute to 1 liter.   Standardize

    against 0.025 N $K_2Cr_2O_7$ as follows: Pipette exactly 25 ml. 0.025

    N $K_2Cr_2O_7$ (11) into a 500 ml. beaker containing 100 ml. distilled

    water, 5 ml. concentrated HCl, 1.2 grams KI. Let stand in the

    dark 5 minutes, dilute to 400 ml., and titrate with the thiosulfate;

    add 1 ml. starch solution (15) near end of titration.

$$N \ Na_2S_2O_3 \ = \ \frac{0.625}{ml. \ Na_2S_2O_3}$$

This solution should be restandardized every two weeks.

11. <u>Potassium Bichromate (0.025 N)</u> - Dissolve 1.2259 grams $K_2Cr_2O_7$,

    which have been previously ground and dried at 110° C. in distilled

    water and dilute to 1 liter in a volumetric flask.

12. <u>Potassium Permanganate Solution</u> - Dissolve 6.32 grams $KMnO_4$ in

    distilled water and dilute to 1 liter.   Keep in dark bottle.

13. <u>Manganous Sulfate Solution</u> - Dissolve 480 grams $MnSO_4$. 4 H_2O

    or 400 grams $MnSO_4.2H_2O$ in distilled water, filter, and dilute

    to 1 liter.

14. <u>Alkaline Potassium Iodine Solution</u> - Dissolve 700 grams KOH or

    500 grams NaOH and 150 grams KI in distilled water. Dilute to

    1 liter.

15. <u>Starch Indicator Solution</u> - Mix 1 gram soluble starch in a small

    amount of cold water to form a thin paste. Add with stirring to

    100 ml. boiling distilled water. When cool, add a few drops of

    chloroform.

16. <u>Potassium Chromate Indicator Solution</u> - Dissolve 2.0 grams of K_2CrO_4 in 100 ml. distilled water, add dilute $AgNO_3$ solution (34) until a slight red precipitate of Ag_2CrO_4 appears. Allow precipitate to settle, filter, and use filtrate for indicator solution.

17. <u>Ammonia Solution (1 to 5)</u> - Dilute one part reagent grade ammonium hydroxide (sp. gr. 0.90) with 5 parts distilled water.

18. <u>Sodium Diethyldithiocarbamate</u> - Dissolve 0.1 gram sodium diethyldithiocarbamate in 100 ml. distilled water. Keep in dark bottle.

19. <u>Sodium Hydroxide (0.2 N)</u> - Dissolve 8.0 grams NaOH in freshly boiled distilled water and make to 1 liter. Standardize by titration against a carefully weighed 1.0 to 2.0 gram portion of potassium biphthalate.

$$N \text{ NaOH} = \frac{(g. \text{ biphthalate}) (4.897)}{Ml. \text{ NaOH}}$$

20. <u>Calcium Chloride Solution</u> - Dissolve 7.55 grams $CaCl_2$ (anhydrous) in distilled water and make up to 100 ml.

21. <u>Borate solution</u> - Dissolve 7.44 grams boric acid in exactly 500 ml. of 0.2 N NaOH (41) and make up to 1 liter with distilled water.

22. <u>Ammonium Molybdate Solution</u> - Dissolve 10.0 grams finely ground $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in distilled water and make to 100 ml.

23. <u>Hydrochloric Acid (Approx. 6.3 N)</u> - Add 60 ml. concentrated HCl to 40 ml. distilled water.

24. <u>Ammonium Molybdate Solution</u> - Solution A: Dissolve 125 grams $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 240 ml. distilled water. Add 140 ml. concentrated NH_4OH, 60 ml. concentrated HNO_3. Solution B: Dissolve 400 ml. concentrated HNO_3 in 960 ml. distilled water and cool to room temperature. Add Solution A to Solution B. Let stand 24 hours and filter if necessary.

25. <u>Nitric Acid (Approx. 1%)</u> - Dissolve 10 ml. concentrated HNO3 in 500 ml. distilled water.

26. <u>Potassium Nitrate Solution (1%)</u> - Dissolve 5 grams KNO3 in 500 ml. distilled water.

27. <u>Phenolphthalein Indicator Solution</u> - Dissolve 1.0 gram phenolphthalein in 200 ml. 50% alcohol. (To make 50% alcohol, dilute 105 ml. 95% alcohol to 200 ml. with distilled water.)

28. <u>Methyl Orange Indicator</u> - Dissolve 0.5 gram methyl orange in 1 liter of distilled water.

29. <u>Hydrochloric Acid (0.5 N)</u> - Add about 43.0 ml. concentrated HCl to 500 ml. distilled water and make to 1 liter. Standardize against standard NaOH solution (19) using phenolphthalein (27) as an indicator.

$$N\ HCl = \frac{(Ml.\ NaOH)\ (N\ NaOH)}{Ml.\ Acid}$$

30. <u>Barium Chloride (10%)</u> - Dissolve about 100 grams C.P. barium chloride in distilled water and dilute to 1 liter.

31. <u>Sulfuric Acid (0.02 N)</u> - Fill a calibrated five gallon bottle to the 18 liter mark with distilled water. Add 10 ml. concentrated H_2SO_4 and mix thoroughly. Titrate against accurately standardized 0.02 to 0.04 N NaOH solution and adjust volume so that the resulting acid solution will have a normality of 0.02.

32. <u>Sodium Hydroxide (Approx. 0.02 N)</u> - Dissolve analytical reagent grade NaOH in distilled water in the proportion of 0.8 grams per liter of solution.

33. <u>Potassium Oxalate Solution (2%)</u> - Dissolve 20 grams $K_2C_2O_4 \cdot H_2O$ in 1 liter of distilled water.

34. <u>Silver Nitrate Solution (0.0172 N)</u> - Dissolve exactly 2.9220 grams silver nitrate in distilled water and make to 1 liter in a volumetric flask. Keep in dark bottle.

35. <u>Ammonium Molybdate Solution</u> - Dissolve 8.2 grams of ammonium molybdate in 200 ml. distilled water. In another container dissolve 41 ml. concentrated H_2SO_4 in 500 ml. distilled water. Add the acid solution to the molybdate solution, mix thoroughly, and make to one liter with distilled water.

36. <u>Stannous Chloride (Concentrated Solution)</u> - Dissolve 112.825 grams $SnCl_2$ in 1 liter concentrated HCl.

37. <u>Stannous Chloride (Dilute Solution)</u> - Dilute 5.0 ml. of concentrated stannous chloride solution (36) to 100 ml. with distilled water.

38. <u>Stock Soap Solution</u> - Dissolve 80-100 grams pure powdered castile soap in 1 liter of 80% ethanol, let stand overnight and decant. Determine lather factor by adding stock soap solution drop by drop from a burette to a 50 ml. portion of freshly boiled and cooled distilled water contained in an 8 oz. sample bottle, shaking between additions. When sufficient soap solution has been added to produce a lather which remains over the entire surface of the water for 5 minutes, record the ml. of soap solution used as the lather factor (L.F.).

39. <u>Standard Soap Solution</u> - Pipette 25 ml. standard calcium carbonate solution (40) and 25 ml. freshly boiled and cooled distilled water into 8 oz. sample bottle, and titrate to a 5 minute lather with stock soap solution. Let "K" represent ml. stock soap solution used. Then 40 (K - L.F.) = X. Dilute X ml. stock soap solution to 1 liter with 80% ethanol prepared by diluting 840 ml. 95% ethanol to 1 liter with distilled water. This is known as the standard soap solution. Determine lather factor for standard soap solution in the same manner as for stock soap solution (38) and record value on bottle.

40. <u>Standard Calcium Carbonate Solution</u> - Dissolve exactly 0.5000 grams pure calcium carbonate in about 5 ml. of approximately 3 N HCl (6). Add about 40 ml. freshly boiled and cooled distilled water and add NH_4OH until slightly alkaline to litmus. Make to exactly 500 ml. with freshly boiled and cooled distilled water. One ml. = 1 mg. $CaCO_3$. Hardness 1.0 p.p.m.

41. <u>Methyl Red Indicator Solution</u> - Dissolve 0.1 gram methyl red in 60 ml. alcohol. Dilute to 100 ml. with distilled water.

RECIRCULATING WATER ANALYSES

I. Determination of Metaphosphate (PO_3^-)

This determination of metaphosphate is based upon a conversion of metaphosphate (PO_3^-) to phosphate (PO_4^{-3}) by refluxing with sulfuric acid. The total phosphate is then determined by adding molybdic acid, reducing the phosphomolybdic acid with hydroquinone, and determining the molybdenum blue colorimetrically. Phosphate is determined in a like manner on an unboiled water sample and the value obtained subtracted from the total phosphate.

Run all tests in duplicate.

Procedure:

1. Filter sample through Whatman paper No. 42 (or equivalent).

2. Pipette 50 ml. filtered sample into 200 ml. Erlenmeyer flask and add 10 ml. 4.3 N H_2SO_4 (1).

3. Reflux for four hours and allow to cool to room temperature.

4. Transfer very carefully to 250 ml. volumetric flask.

5. Add 5 ml. molybdic acid solution (5) and 5 ml. 2% hydroquinone solution (3).

6. Allow to stand 5 minutes and add 15 ml. carbonate-sulfite reagent (4) and shake until effervescing ceases.

7. Make to 250 ml. mark with 2 N H_2SO_4 (2).

8. Using red filter, (C, 610 mu) read transmission on Photelometer using distilled water for blank.

9. Find p.p.m. total PO_4^{-3} from Figure 1.

10. Repeat procedure omitting step 3 to get p.p.m. original PO_4^{-3}.

11. Ppm PO_3^- = 0.83 (p.p.m. total PO_4^{-3} - p.p.m. original PO_4^{-3}.

II. Determination of Solids

A. Suspended Solids

1. Shake water sample until homogeneous.

2. Filter 100 ml. sample through a tared fritted Gooch filter.

3. Dry two hours in oven at about 103° C. and weigh.

4. P.p.m. suspended solids = ("Wt. gain in g.) (10,000).

B. Total Dissolved Solids

1. Evaporate without actively boiling, 100 ml. filtered sample in a tared 250 ml. beaker or Erlenmeyer flask.

2. Dry for 2 hours in oven at 103° C. and weigh.

3. P.p.m. total dissolved solids = ("Wt. gain in g.) (10,000).

C. Total Solids

1. P.p.m. total solids = p.p.m. suspended solids ≠ p.p.m. dissolved solids.

III. Determination of Total Iron

This colorimetric determination of iron is based upon the formation of a very stable colored complex by ferrous iron and ortho-phenanthroline. The concentration of iron is determined by use of a graph.

Procedure:

1. Add 1-2 ml. concentrated HNO_3 to 100 ml. of sample and evaporate to dryness.

2. To the residue add 1-2 ml. 3 N HCl (6) and warm on water bath until residue is dissolved. Avoid evaporation to dryness by addition of small amounts of water if necessary.

3. When dissolved, dilute with a small amount of water (10-15 ml.), filter into a 100 ml. volumetric flask, washing filter with several small portions of water.

4. Add 1.0 ml. 10% hydroxylamine hydrochloride solution (7).

5. Mix and allow to stand 1-2 minutes.

6. Add distilled water to bring volume to approximately 50 ml.

7. Add 10 ml. 0.1% O-phenanthroline solution (8) and mix.

8. Add 10 ml. 30% ammonium acetate solution (9) and mix.

9. Dilute to mark with distilled water and mix.

10. Using blue filter (A, 410 mu) read percentage transmission on Photelometer using distilled water for blank.

11. Read p.p.m. iron directly from Figure 2.

IV. Determination of Dissolved Oxygen

This determination is based upon the dissolved oxygen uniting with manganous sulfate under the conditions of the test to give manganic sulfate. The manganic sulfate releases iodine from potassium iodide. The iodine is titrated with sodium thiosulfate using starch as an indicator. Collection of sample: Use a sampling device provided for this purpose.

Procedure:

1. Place completely filled sample bottle in a bucket containing same water as sample. The top of sample bottle must be well beneath the surface of the water.

2. Remove stoppers carefully and add to the sample in the bottle beneath the surface of water, 0.7 ml. concentrated H_2SO_4 and 1 ml. $KMnO_4$ solution (12).

3. Insert stopper and mix by inverting sample bottle.

4. Allow to stand 20 minutes.

5. If a noticeable excess of $KMnO_4$ is not present, add 1 ml. more of $KMnO_4$ solution (12).

6. Let stand 20 minutes and destroy excess $KMnO_4$ with 1 ml. $K_2C_2O_4$ solution (33).

7. Add 1 ml. $MnSO_4$ solution (13) and mix. Then add 3 ml. alkaline KI solution (14).

8. Allow ppt. to settle, add 1 ml. concentrated H_2SO_4 and mix well.

9. Remove sample bottle from bucket or tank, measure out 200 ml., and titrate with $Na_2S_2O_3$ solution (10) using starch (15) as indicator near end of titration.

10. P.p.m. dissolved oxygen $= \dfrac{(\text{Ml. } Na_2S_2O_3)\ (\text{Normality } Na_2S_2O_3)}{0.025}$

V. Determination of Silica

This determination is based upon the formation of yellow silico-molybdic acid, a highly colored substance suitable for colorimetric analyses when silica reacts with ammonium molybdate.

Procedure:

1. To 100 ml. of water sample add 50 ml. borate mixture (21) and 2 ml. $CaCl_2$ solution (20).

2. Stir vigorously and allow to stand for one hour.

3. Filter through Whatman's paper No. 42 (or equivalent).

4. Pipette 50 ml. of the filtrate into a beaker, add 50 ml. distilled water.

5. Add 2 ml. ammonium molybdate solution (22) and 1 ml. HCl solution (23).

6. Allow to stand 10 minutes, then read the percentage transmission on the Photelometer. Use the blue (A, 410 mu) filter and use distilled water for comparison.

7. Read p.p.m. silica (SiO_2) directly from Figure 3.

VI. Determination of Copper

Addition of sodium diethyldithiocarbamate to an ammonical solution of cupric salt in dilute solution produces a brownish yellow colloidal suspension suitable for colorimetric comparison.

Procedure:

1. Filter 75-100 ml. of water through a Whatman's paper No. 42. (The filtrate must be refiltered if necessary until clear).

2. To 50 ml. of filtered water add 5 ml. of ammonium hydroxide reagent (17).

3. Then add 5 ml. sodium diethyldithiocarbamate solution (18), and mix well.

4. Read on Photelometer using a blue filter (A, 410 mu) using a filtered portion of the original sample as a blank.

5. Determine the p.p.m. of copper from Figure 4.

BOILER WATER ANLYSES

I. Determination of Total Dissolved Solids

Procedure:

1. Filter a representative sample of water through Whatman's paper No. 42 (or equivalent).

2. Pipette 100 ml. filtered sample into a tared 250 ml. beaker or flask.

3. Evaporate almost to dryness on hot plate, avoiding active boiling.

4. When almost dry, place beaker in oven at 103° C. for two hours.

5. Cool in desiccator and weigh.

6. P.p.m. total dissolved solids (TDS) = (Wt. gain in g.) (10,000).

II. Determination of Sulfate

Procedure:

1. Measure 200 ml. filtered water into 400 ml. beaker.

2. Add 2-5 drops of methyl red (41) or methyl orange indicator (28).

3. Add concentrated HCl until indicator is red, then add about 0.5 ml. in excess. Avoid a large excess of HCl as it increases the solubility of the barium sulfate.

4. Evaporate to about 100 ml.

5. To the hot solution, add slowly and with stirring 10 ml. 10% $BaCl_2$ solution (30). Avoid rapid addition of $BaCl_2$ solution to prevent co-precipitation of the chloride.

6. Keep hot (just below boiling) for one hour or until the precipitate grains out and goes to bottom.

7. Filter through Whatman's filter paper No. 42, being very careful to remove the last traces of precipitate from the beaker. Be sure no precipitate passes the filter.

8. Wash precipitate several times with small portions of distilled water. Do this washing carefully going downward from top of filter paper.

9. Transfer filter paper with precipitate to clay annealing cup, set in door of muffle furnace heated to 700° C. with door open until paper has burned off,

10. After paper has burned off, close furnace and ignite for one hour. Cool in desiccator.

11. Transfer precipitate to tared watch glass and weigh.

12. P.p.m. $SO_4^{-2} = (2057.5)$ (g. $BaSO_4$).

Alternative: If preferred by the operator, the precipitate may be burned in a tared glazed crucible which will be reweighed after ignition and cooling to determine weight of $BaSO_4$.

III. Determination of "P" and "M" Alkalinity

and Sodium Chloride

A.. In this determination "P" and "M" alkalinities are determined by titration to phenolphthalein and methyl orange end points respectively. The NaCl is determined volumetrically by titration with $AgNO_3$.

Procedure:

1. Filter through Whatman's paper No. 42.

2. Pipette 50 ml. filtered sample into Erlenmeyer flask and add 3 drops phenolphthalein solution (27).

3. Titrate to end point with 0.02 N H_2SO_4 (31).

4. Record ml. acid used as "P" end point.

5. Add three drops methyl orange indicator solution (28) to the same sample.

6. Continue titration to the methyl orange end point (light orange).

7. Record total ml. acid used as "M" end point.

8. P.p.m. "P" alkalinity = (ml. 0.02 N H_2SO_4 to "P") (20).

9. P.p.m. "M" alkalinity = (ml. 0.02 N H_2SO_4 to "M") (20).

10. Save sample for part B.

B. Determination of Sodium Chloride

1. Back titrate the "P" and "M" sample with NaOH until just pink to phenolphthalein and make just acid again with H_2SO_4.

2. Add one ml. K_2CrO_4 indicator solution (16).

3. Titrate with 0.0172 N $AgNO_3$ (34) until the red coloration of silver chromate appears. Record the ml. of silver nitrate used.

4. Run a blank by titrating 50 ml. of distilled water with 0.0172 N $AgNO_3$ (34) using 1 ml. K_2CrO_4 (16) as indicator. The number of ml. $AgNO_3$ used to give the red coloration is the blank.

5. Ppm. NaCl = (ml. $AgNO_3$ - blank((20).

ANALYSIS OF PIPE WASH SOLUTION - SEELEY'S SINK

This is a method for the determination of phosphate, carbonate, and hydroxide in solution. The phosphate is determined gravimetrically and the carbonate and hydroxide by titration with standard acid.

I. Determination of Phosphate

Procedure:

1. Measure 10.0 ml. of filtered sample from a pipette into a 400 ml. beaker and neutralize with HNO_3.

2. Dilute to about 100 ml. with distilled water and add 5 ml. concentrated HNO_3.

3. Adjust volume to about 150 ml. with distilled water.

4. Heat to 60° C., add 100 ml. ammonium molybdate solution (24) and stir vigorously until the precipitate forms.

5. Keep warm for one hour, allowing precipitate to settle.

6. Filter through a dry, tared, Gooch or sintered glass crucible.

7. Test filtrate by adding small amount of ammonium molybdate (24) to see if more precipitate is formed. If so, filter again and repeat test until no more precipitate is formed.

8. Wash the precipitate twice with 1% HNO_3 (25) and once with 1% KNO_3 (26).

9. Dry for two hours at 100° C. Cool in desiccator and weigh.

II. Determination of Carbonate and Hydroxide

Procedure:

1. Pipette 25 ml. unfiltered sample into a 250 ml. Erlenmeyer flask.

2. Add 2 drops phenolphthalein indicator.

3. Titrate to disappearance of red color with 0.5 N HCl (29).

4. Record ml. 0.5 N HCl (29) used as "P" end point.

5. Add 3 drops methyl orange indicator solution and continue titration to the methyl orange end point.

6. Record total ml. 0.5 N HCl used as "M" end point.

7. Subtract ml. 0.5 N HCl used to "P" and point from ml. 0.5 N. HCl used to "M" end point. This value is (M-P).

8. Oz./gal. Na_3PO_4 = (wt. ppt.) (0.0874) (100) (0.1335),

   oz./gal. Na_3PO_4 = (wt. ppt.) (1.1661).

$$Oz./gal.\ Na_2CO_3 = (0.1335)\ (0.053)\ (2)\ (0.5)\ (40)\ \frac{[(M-P)-(wt.\ ppt.)(2.5)]}{(1.877)\ (0.5)}$$

$$Oz./gal.\ Na_2CO_3 = 0.283\ [(M-P - (wt.\ ppt.)\ (2.67)]$$

$$Oz./gal.\ NaOH = [P-(M-P)]\ [0.5]\ [0.04]\ [40]\ [0.1335]$$

$$Oz./gal.\ NaOH = 0.1068\ [P-(M-P)]$$

Figure 1
Phosphate
By Hydroquinone Reduction
Of Phosphomolybdic Acid
Cenco Photelometer
Red Filter - 610μ
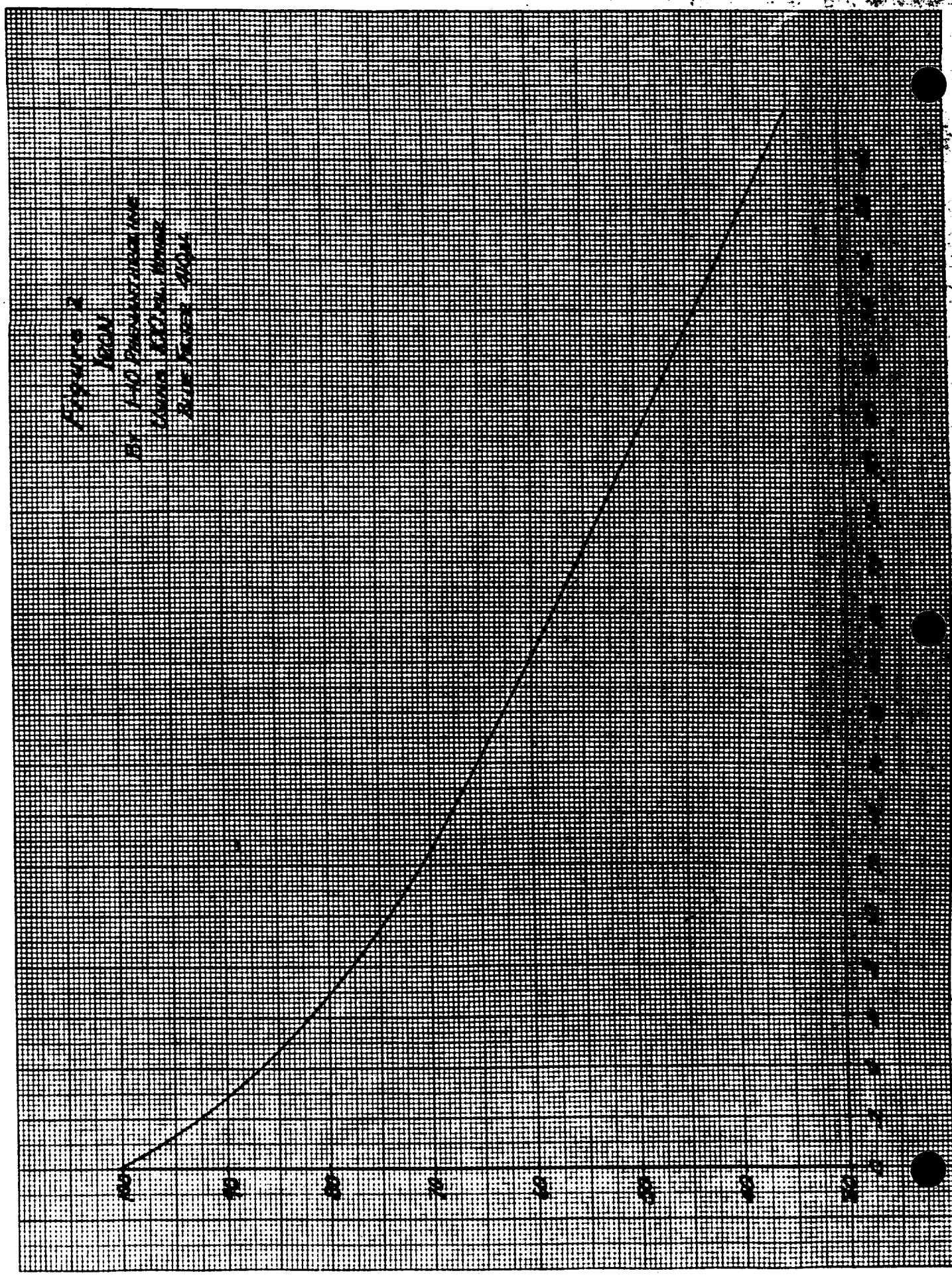
Figure 2

Figure 3

Determination of Silica
by Formation of Silicomolybdate
Blue Filter 440μ

% Transmission

100

90

80

PPM SiO₂

EUGENE DIETZGEN CO.
MADE IN U.S.A.

NO. 340-10 DIETZGEN GRAPH PAPER
10 X 10 PER INCH
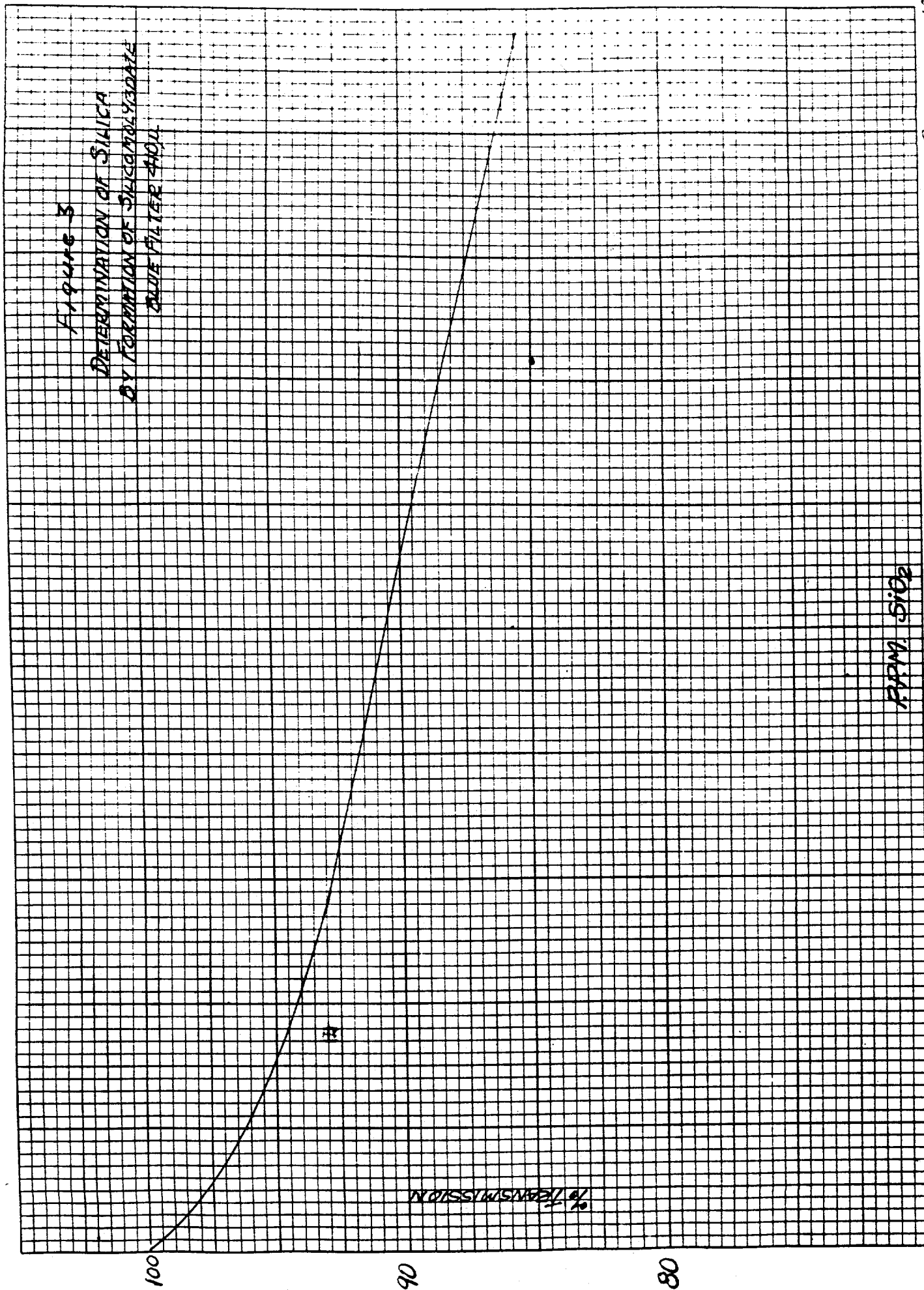
Figure 4
Copper
By Sodium Diethyl Dithiocarbamate
using 50 ml. on Filtered Water
Blue Filter 410μ

% TRANSMISSION

P.P.M. Cu #

DETERMINATION OF MOISTURE IN CARBON

I. Apparatus

    A. Oven capable of maintaining a temperature of 150° C.

    B. Glass weighing bottles with tops.

II. Procedure

    A. Weigh quickly a 2 to 4 g. sample into a tared glass weighing bottle with top.

    B. With top removed, dry in oven at 150° C. for 2 hours.

    C. Remove from oven and replace top.

    D. Cool in a desiccator and reweigh quickly.

III. Calculations

$$\frac{(\text{Loss in weight}) \,(100)}{\text{Weight of sample}} = \% \text{ moisture}$$

DETERMINATION OF MOISTURE IN ALUMINA

I. Apparatus

Muffle furnace

Coal moisture dishes with aluminum covers.

II. Procedure

A. Weigh quickly a 2 to 4 g. sample into a tared coal moisture dish. (Do not weigh the cover).

B. Dry sample in muffle at 900° F. for one hour.

C. Remove from oven and cool in desiccator with cover in place.

D. When cool remove top and weigh quickly.

III. Calculations

$$\frac{(Loss\ in\ weight)\ (100)}{Weight\ of\ sample} = Per\ cent\ moisture$$

DETERMINATION OF DEW POINTS WITH

LUCITE DEW POINT METER

This is a method for the determination of low temperature dew points using a portable dew point meter.

I. Apparatus

A. The dew point meter is made up of the following parts shown in Figure 1.

1. Meter Box - The meter box is made of lucite tubing painted black. The top and bottom are lucite; the top is clear while the bottom is painted black. There are four holes in the box, one for the orifice, one for the cold finger, one for the light, and one for the exhaust.

2. Orifice - The orifice is made of 1/8 in. copper tubing silver soldered to a 1/4 in. male flare to 1/4 in. male pipe union. The copper tubing is approximately 3/4 in. long, but this length may vary.

3. Cold Finger - The cold finger is made of a 1/4 in. copper tube 6 in. long with a copper disc 1/8 in. thick and approximately 9/16 in. in diameter soldered to the end. The 1/4 in. copper tubing is silver soldered into a 1/4 in. to 5/8 in. sweat coupling to which a 5/8 in. copper tubing 1-1/4 in. long has been silver soldered. The 1/4 in. copper tubing extends through the inside of the 5/8 in. copper tubing, and is placed so that the distance between the top of 5/8 in. copper tubing and the plate is approximately 1/8 in.

Running through the 1/4 in. copper tube, and soft soldered to the top of the copper plate is a No. 24 gauge constantan wire. A 1/32 in. platinum plate is soldered to the copper disk so that it makes contact with the constantan wire at this point. The platinum is highly polished after being soldered to the copper plate. On the side of the 1/4 in. copper tube at the point it passes through the 1/4 in. to 5/8 in. coupling, a No. 24 gauge copper thermocouple wire is soldered. The constantan wire is soldered to a copper wire to form the reference junction. The two copper wires are soldered into a female amphenol plug for connection to the pyrometer.

4. Light Finger - The light projector is made of lucite. This has an opening at one end large enough to enclose a 2.5 volt light bulb and socket. The connections to this bulb are soldered into a male jack plug. The other end of the finger is about 1/8 in. in diameter and goes into the lucite box. It extends just to the edge of the platinum plate, so that the light shines on the plate at such an angle that the light appears only when the dew or moisture appears on the plati-num plate.

The battery for the light is a 1.5 volt battery. The connections from the battery are soldered into female jack plugs. An arrow H and H single pole toggle switch controls this light.

5. Rotameter - The rotameter and bob are made of lucite. The inside of the tube is tapered with the wide part at the top. Both ends of the tube are threaded to fit a 1/4 in. female pipe to 1/4 in. male flare union.

B. Carrying Box - The plywood box in which the meter and other parts are carried is made of 3/8 in. plywood with compartments, for the battery, the dewar for the reference junction, the dewar for the cold finger, the lucite meter, and rotameter. There is also a space in the back for carrying extra dewars, copper tubing, and valves. There is a handle on top of box for carrying.

C. Pyrometer - The pyrometer by which the temperature is measured is a Brown Instrument Co. Model 1001 Indicating Millivolt Pyrometer. An instrument calibrated for the range 0-240° C. with a copper constantan couple is modified and recalibrated so that the range is $\neq$ 32° F. to -200° F. The thermocouple is attached with an amphenol plug to the pyrometer and a short out switch is provided to prevent the needle swinging when the instrument is carried. A separate box is provided for carrying the pyrometer.

D. Assembly of meter - The meter is assembled as shown in Figure 2. The orifice should be about 1/4 in. from the plate. All connections are made with 1/4 in. copper tubing and flare unions. The flow of gas to the meter is controlled by two California valves.

The exhaust is the same diameter as the orifice and passes through the lucite at the same angle as the orifice, within 1/4 in. of orifice opening.

II. Procedure

A. Calibration of the meter

1. Calibrate the lucite rotameter by connecting the exit of the rotameter to a wet test meter and pass nitrogen through both meters at varying rates between 50 ml. and 400 ml. per minute. Mark the calibrations on the rotameter at 50 ml. intervals.

2. Prepare a 1/4 in. copper tube with flare nuts, long enough so as to make 5 complete coils in a large dewar. Place the coils so that the axis of the coil is perpendicular to the axis of the dewar and approximately 5 in. of each coil loop is exposed to the air.

3. Connect one end of this coil to the dew point meter through the California valves and the other end of a cylinder of nitrogen.

4. Fill the dewar with crushed dry ice and trichlorethylene making a slush. Determine the temperature of this bath with a copper-constantan thermocouple with ice reference junction. It should be between -108° to -113° F. The temperature of the nitrogen as it passes through the copper coil will be lowered to within 1° F. of the temperature of the bath.

5. Immerse the reference junction of the thermocouple in a dewar containing ice and distilled water.

6. Fill a small dewar with L-28 and immerse the cold finger in it. The rate of cooling of the cold finger may be controlled by the depth to which the cold finger is immersed in the coolant. The rate of cooling has no effect on the dew point.

7. By manipulation of valves 1 and 2, regulate the flow of nitrogen through the meter as near as possible to 250 ml. per minute.

8. Adjust the distance between the orifice and the platinum plate so that it will be approximately 1/4 in.

9. After obtaining a constant flow of 250 ml. per minute, watch for the fog to appear on the plate. If it appears before the temperature has come to within 1° of the temperature of the slush, the orifice and the plate are too close together and should be spaced farther apart. If the fog appears at a temperature lower than the slush temperature, the orifice and the plate are too far apart and should be brought closer together. When the orifice and plate have been spaced so that the dew point temperature and the slush temperature are the same the meter is calibrated.

10. In case the light does not "spot" the fog, adjust the lucite light holder to the position that will give the best results, this may be done by bringing the light either nearer or farther from the plate.

11. Once the meter is calibrated, the flow is not critical and can be varied between 50 ml. per minute and 400 ml. per minute without affecting the results.

12. If the meter is to be used in the sun light, the best results may be obtained by covering the meter box to prevent the sun light from striking the top of the meter. The meter light will not show on the platinum plate in the presence of bright light.

13. If the temperature reading drops rapidly and falls to the lowest reading, there is a short circuit in the thermocouple (i.e. the copper tubing is in contact with the constantan wire between the contact point on the plate and the reference junction.)

B. Determination of Dew Point

1. Immerse the reference junction in a dewar containing ice and water.

2. Attach the gas to be sampled at valve 1 and regulate the flow to 250 ml. per minute by adjusting valves 1 and 2. Allow gas to flush through the meter for 10-15 minutes.

3. Fill another dewar with L-28 and immerse the cold finger in the coolant.

4. Watch the plate very carefully until a spot of frost appears on the meter and note the temperature of the dew point on the pyrometer.

5. Remove the L-28, allow the meter to warm to /32° F. and repeat the determination.

TOP VIEW

←OPENING FOR ORIFICE

←OPENING FOR EXHAUST

OPENING FOR COLD FINGER

←OPENING FOR LIGHT
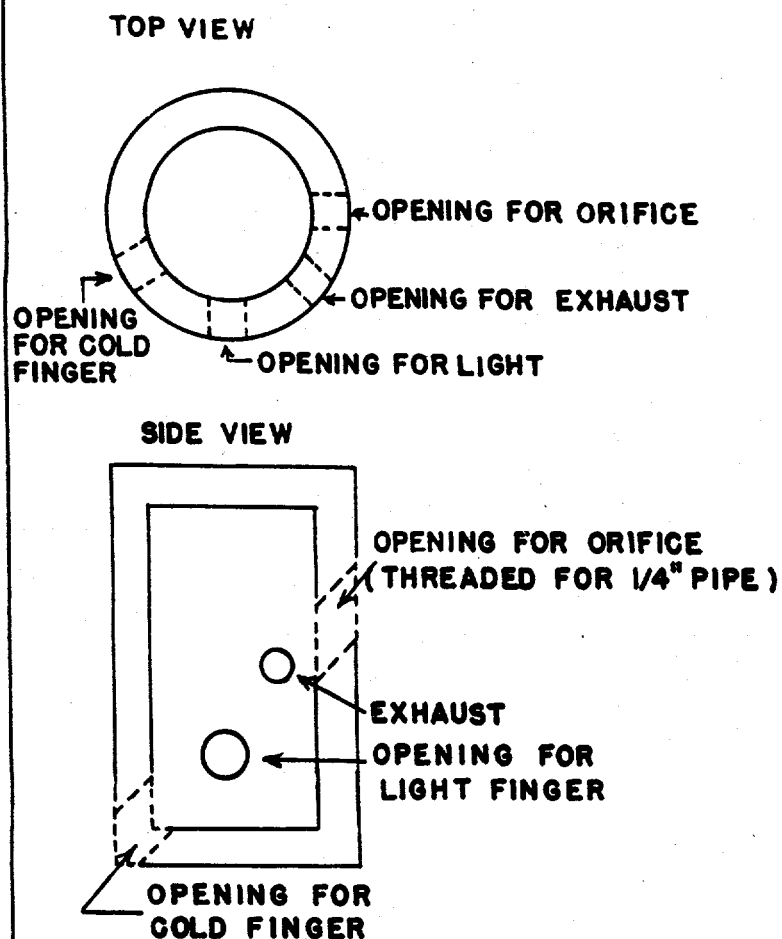
FIGURE I
PARTS FOR LUCITE
DEW POINT METER

SIDE VIEW

OPENING FOR ORIFICE
(THREADED FOR 1/4" PIPE)

EXHAUST
OPENING FOR
LIGHT FINGER

OPENING FOR
COLD FINGER

A. LUCITE METER BOX

1/4" FLARE

1/4" PIPE

←1/8" COPPER TUBE

B. ORIFICE

WELL FOR
THERMOCOUPLE

1/4" COPPER
TUBING

1/4"- 5/8" SWEAT
COUPLING

5/8" COPPER
TUBING

1/32" PLATINUM
PLATE
SOFT SOLDERED
TO COPPER

C. COLD FINGER

THREADED TO FIT
SOCKET FOR
2.5V BULB

THREADED TO FIT 1/4" FEMALE
PIPE FITTING
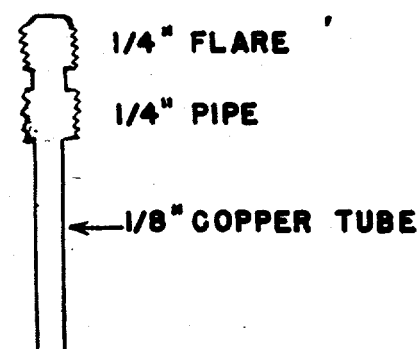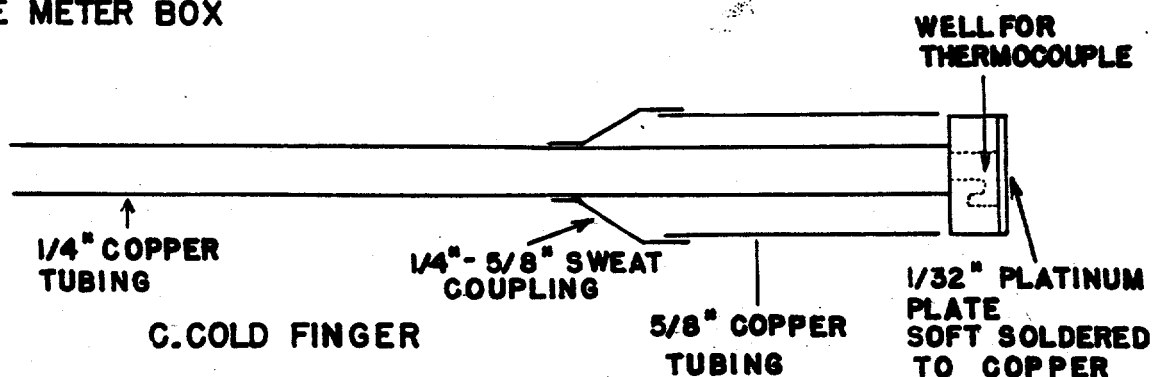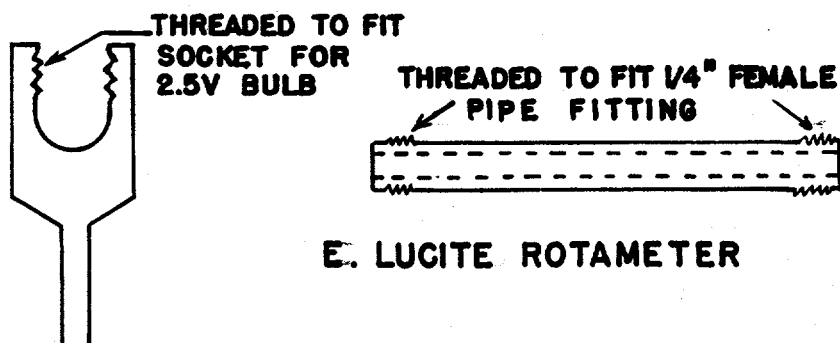
E. LUCITE ROTAMETER

F. LUCITE BOB
FOR ROTA-
METER

D. LUCITE LIGHT FINGER

TOP VIEW

FIGURE 2
ASSEMBLY
LUCITE DEW POINT
METER

ORIFICE (B)

COLD FINGER (C)

EXHAUST

LIGHT FINGER (D)

1/4" COPPER

EXHAUST

ORIFICE (B)

1/4" FLARE

1/4" PIPE

LUCITE
ROTAMETER (E)

LIGHT FINGER (D)

COLD FINGER (C)

THERMOCOUPLE
—— COPPER
----CONSTANTAN

WASTE

CALIF.
VALVES

2

1

SAMPLE

AMPHENOL
PLUG FEMALE TO
PYROMETER

COLD
JUNCT.
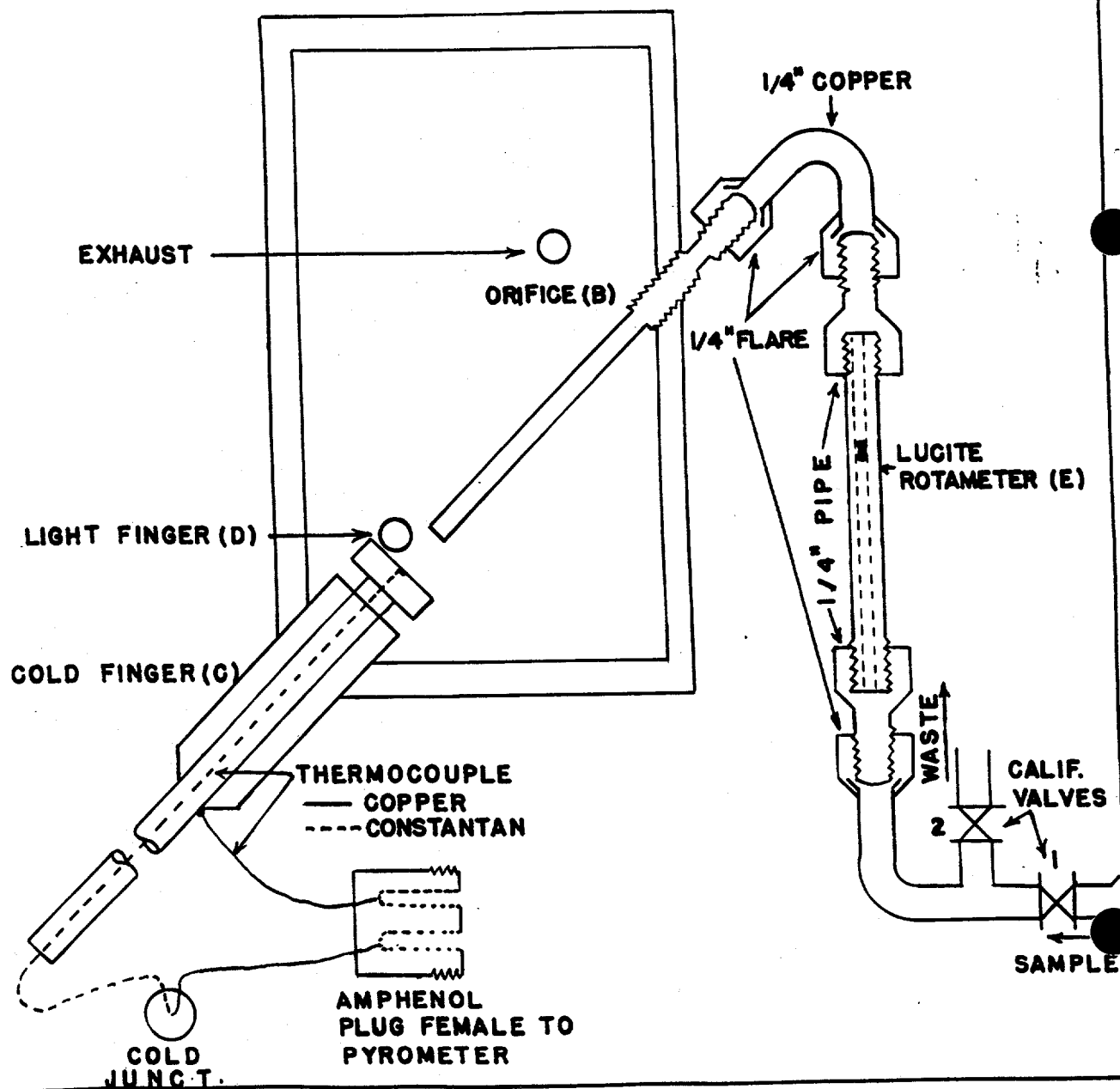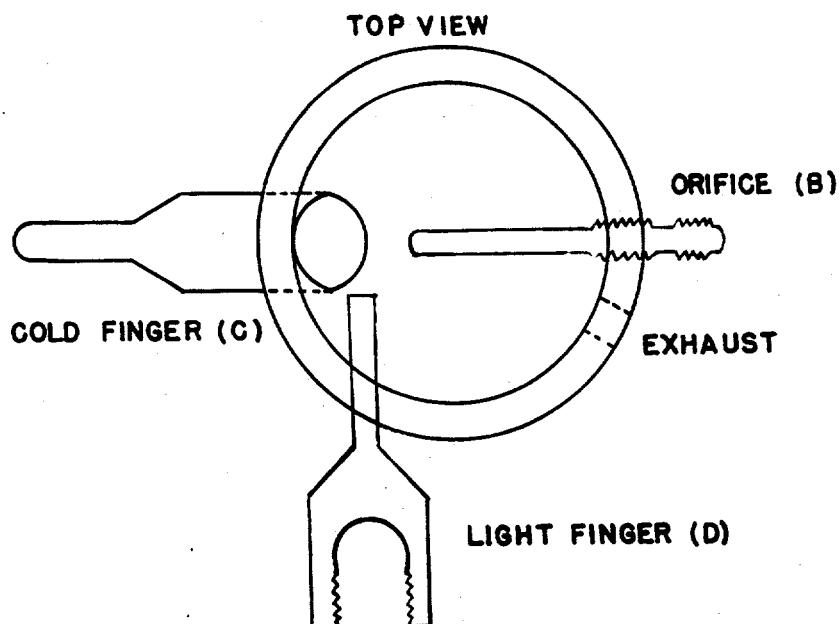
METHODS OF ANALYSIS FOR SOLUTIONS USED IN THE CLEANING AREA

Tank H-306

5 Parts by Volume HCl.

To Determine Total Acidity:

Pipet 25 ml. sample into a 250 ml. Erlenmeyer flask and dilute with distilled water to 150 ml.; add 2 drops methyl orange. The solution will be pink. Add 0.5 N NaOH from a buret until the end point is reached. (The color will change from pink to amber upon the addition of ONE drop of NaOH). Record the volume of NaOH used on a report sheet. Make final report (using graph H-306) as "parts by volume 20° Bé HCl". Allowable limits 4-6 parts/vol.

Tank H-304-A

15 Parts by Volume HCl.

To Determine Total Acidity:

Pipet 10 ml. sample into a 250 ml. Erlenmeyer flask and dilute with distilled water to 150 ml.; add 2 drops methyl orange. The solution will be pink. Add 0.5 N NaOH from a buret until the end point is reached. (The color changes from pink to amber upon the addition of ONE drop of NaOH). Record the volume of NaOH used on a report sheet. Make final report (using graph H-304-A) as "parts by volume 20° Bé HCl". Allowable limits 14-16 parts/vol.

Tank H-304-B, Tank E-302, and Tank H-305

35 Parts by Volume HCl.

To Determine Total Acidity:

Pipet 5 ml. sample into a 250 ml. Erlenmeyer flask and dilute with distilled water to 150 ml.; add 2 drops methyl orange. The solution will be pink. Add 0.5 N NaOH from a buret until the end point is reached. (The

color changes from pink to amber upon the addition of ONE drop of NaOH). Record the volume of NaOH used on a report sheet. Make final report (using graph H-304-B) as "parts by volume 20° Bé HCl". Allowable limits 32-37 parts/vol.

Tank H-307

5 Parts by Volume H_2SO_4.

4 Ounces per Gallon $Na_2Cr_2O_7$.

The analysis of this tank is divided into two parts:
The first in which total acidity of the tank is determined and, the second in which the dichromate ($Na_2Cr_2O_7$) content is determinded.

(A) To determine total acidity:

Pipet a 10 ml. sample into a 50 ml. beaker. Add 30 ml. 0.5 N NaOH with constant stirring. Check pH on the pH meter. If the pH is below 4, add more NaOH in drops until a pH of 4 is reached. When a 4 pH is reached, record volume of NaOH used. Make final report (using graph H-307 for H_2SO_4) as "parts by volume 66° Bé H_2SO_4". Allowable limits 4.5-5.5 parts/vol.

Note: If the pH is above 4 on the first measurement with pH meter, take a new sample and add less than 30 ml. NaOH, depending upon the pH indicated by the meter.

(B) To Determine Dichromate Content.

(1) Preliminary - Add 50 ml. 0.1 N $FeSO_4$ to a 250 Erlenmeyer flask from a buret. Titrate this sample with 0.1 N $KMnO_4$. At the end-point the clear $FeSO_4$ solution will turn to a light pink color upon the addition of one drop. Record the volume of $KMnO_4$ used. (Daily Standard Sheet).

(2) Final - Pipet a 5 ml. sample of H-307 into a 250 ml. Erlenmeyer flask. Add 50 ml. 0.1 N $FeSO_4$ from a buret and shake. Now titrate with

0.1 N $KMnO_4$ until the end point (a $KMnO_4$ coloration in the gray solution) is reached. Subtract the mls. $KMnO_4$ used in this titration from the ml. $KMnO_4$ used in the preliminary titration and record the difference on the report sheet. Make the final report (using graph H-307 for $Na_2Cr_2O_7$) as "ounces per gallon $Na_2Cr_2O_7$". Allowable limits 3.5 to 4.5 oz./gal.

Tank H-303 and Tank E-309-A

6-8 Ounces per Gallon CSR Cleaner.

To Determine Total Alkalinity.

Pipet a 25 ml. sample into a 250 Erlenmeyer flask and dilute with distilled water to 150 ml. Add 2 drops phenolphthalein indicator. The solution will be pink. Titrate with 0.5 N HCl to the end-point (the solution will turn colorless upon the addition of ONE drop of HCl). Record mls. HCl used on report sheet. Make final report (using graph H-303) as "ounces per gallon CSR Cleaner". Allowable limits 6-8 oz./gal.

Tank H-302-A and Tank E-303-A

6 Fluid Ounces per Gallon Ammonia.

To Determine Total Alkalinity.

Pipet a 25 ml. sample into an Erlenmeyer flask and dilute with distilled water to 150 ml. Add 2 drops of methyl red indicator. The solution will be amber. Titrate with 0.5 N HCl until one drop of HCl will change the color to pink. Record ml. HCl used on the report sheet. Make final report (using graph H-303-A) as 'fluid ounces $26°$ Bé NH_4OH per gallon.' Allowable limits 5-7 fl. oz./gal.

D-301 Degreaser.

To Determine pH.

Using a pint bottle remove approximately equal volumes of degreaser solvent from both ends of the tank. Take 100 ml. of the solvent and 100 ml. of distilled water and put in separatory funnel. Insert the ground glass stopper and shake well to mix contents thoroughly. Allow to stand for at least 15 minutes. By means of the stopcock allow the dark lower layer to run off into the sink drain. Pour some of the liquid remaining in the funnel into a 50 ml. beaker until the beaker is approximately 2/3 full. Using the pH meter, determine the pH and record the result on the report sheet.

Note: Leave electrodes immersed in the liquid for only a very short time. As soon as the pH is determined, remove the electrodes from the liquid and wipe off immediately.

For All Water Tanks:

Determine turbidity and pH of these samples. Record the results of these determinations on the report sheet.

For Water Filters and Sanitary Water:

Determine turbidity and pH on these samples and record results on report sheet.

For Effluent Drain:

Determine pH by using pH meter.

All SC-10 Tanks

10 Parts by Volume Sodium Carbonate.

To Determine Total Alkalinity:

Pipet a 10 ml. sample into an Erlenmeyer flask and dilute to 150 ml. with distilled water. Add 2 drops methyl orange indicator. The solution will be yellow. Titrate with 0.5 N HCl until the end-point is reached. (The color changes from yellow to burnt orange upon the addition of ONE drop of HCl). Record the mls. HCl used on a report sheet. Make final report (using graph for SC-10) as percent Na_2CO_3.

Determine pH on these samples by using pH meter.

Tank W-11

Rinse Tank.

To Determine Total Alkalinity:

Pipet a 100 ml. sample into an Erlenmeyer flask and dilute with distilled water to 150 ml.

Follow procedure for SC-10 tanks. Use graph for W-11.

Determine pH by using pH meter.

DETERMINATION OF IMPURITIES IN CLEANING TANKS

DETERMINATION OF IRON IN CLEANING SOLUTIONS

Put a 10 to 100 ml. sample (according to iron content) into a 600 ml. beaker. Add 2 ml. of 0.5 N stannous chloride solution. Boil for about 2 minutes. From a pipette add enough conc. $KMnO_4$ to produce a yellow color. Quickly drop in stannous chloride until the last drop just discharges the yellow iron color. Add 3 more drops. Let cool for 5 minutes. Add 10 ml. of 0.5 N mercuric chloride solution. Wait 5 minutes. Add 15 ml. of 0.5 N manganous sulfate solution and enough water to almost fill the beaker. Titrate with 0.1 N $KMnO_4$ to a faint pink end point. (The pink color should persist for 15 seconds or longer).

Calculation:

$$\% Fe = \frac{(ml. \ KMnO_4) \ (0.05584) \ (100)}{ml. \ of \ sample}$$

DETERMINATION OF METALS IN CLEANING SOLUTIONS

Hydrochloric Acid Solutions.

A - Iron.

Place a 100 ml. sample in a 400 ml. beaker and add 5 ml. bromine water as an oxidizing agent. Boil the solution until excess bromine has been removed. The color of methyl red indicator is destroyed by the bromine, but when the bromine is removed the indicator will retain its color. Heat solution to about 70° C. and add 6 N ammonium hydroxide until the solution just turns yellow or until a faint odor of ammonia is present. Allow the precipitate to settle; wash several times with hot water by decantation. Transfer the precipitate to the filter with the aid of a rubber policeman.

Wash precipitate on filter with hot 2% ammonium nitrate solution until free from chlorides. Save the filtrate.

Dissolve the precipitate with hot HCl and catch the solution in a clean beaker. Evaporate until just enough HCl remains to hold the iron in solution. Add stannous chloride until solution is completely decolorized, but avoid using an excess of stannous chloride. Cool to room temperature and add 10 ml. mercuric chloride solution (saturated) to remove any excess stannous chloride. Dilute the solution to about 250 ml. after about 5 minutes. Add 20-25 ml. of manganese sulfate-phosphoric acid solution and titrate with 0.1 N potassium permanganate solution to a pink end-point. The coloration should persist for 15 seconds. Take care to add the permanganate a drop at a time near the end-point, allowing the coloration to disappear after each drop is added.

The amount of iron present is calculated as follows:

$$(\text{ml. } 0.1 \text{ N KMnO}_4) \ (0.005584) = \text{g. Fe in sample}$$

B. Copper.

Use the filtrate from the iron determination for the copper determination. Add ammonium hydroxide until ammonia odor is evident in the solution or until it shows an alkaline reaction. Filter the solution and wash until the blue color is removed from the filter paper. Acidify with glacial acetic acid (5-10 ml.). Add 30 ml. 10% potassium iodide solution and 5 ml. starch solution. Titrate the liberated iodine with 0.1 N sodium thiosulfate solution to the point at which one drop destroys the blue color. Note: It is advisable to add 1/2 ml. more of KI solution; if a blue color results add more 0.1 N sodium thiosulfate solution until the color is destroyed.

The amount of copper present is calculated as follows:

$$(ml.\ 0.1\ N\ Na_2S_2O_3)\ (0.006357)\ =\ g.\ Cu\ in\ sample.$$

C. Nickel.

A sample should be taken so that the nickel content does not exceed 0.1 g. A 10 ml. sample should be sufficient for the determination. Add one or two g. tartaric acid to the sample to prevent the precipitation of iron, aluminum or chromium; add 5-10 ml. 10% ammonium chloride solution. Add ammonium hydroxice until the solution shows an alkaline reaction or until the odor of ammonia is evident in the solution. If a precipitate forms, add ammonium chloride solution until the solution remains clear. Heat to nearly boiling and add the alcoholic solution of dimethylglyoxime until this reagent is seven times, by weight, the weight of nickel present. Add ammonium hydroxide until the odor of ammonia is distinctly evident in the solution. Stir to hasten the precipitation of the scarlet-red nickel dimethylglyoxime salt. Place solution on steam bath for fifteen minutes.

Filter the precipitate through a Gooch crucible prepared with an asbestos mat (or through a similar filtering device) and wash the precipitate. Dry the crucible and its contents at 110°-$120^{\circ}C$ in a drying oven for two hours. Weigh the precipitate which contains 20.31% Ni.

The amount of nickel present is calculated as follows:

$$(wt.\ of\ precipitate)\ (0.2031)\ =\ weight\ of\ nickel\ present.$$

SULFURIC ACID – SODIUM DICHROMATE SOLUTIONS

A. Iron,

See procedure 1-A (Iron in HCl Solutions).

Note: Save filtrate from iron ppt.

B. Copper.

See procedure 1-B (Copper in HCl Solutions).

C. Nickel.

See procedure 1-C (Nickel in HCl Solutions).

D. Chromium.

Pipet a 10 ml. sample into a 500 ml. volumetric flask and dilute to mark with distilled water. Mix well. From this flask, pipet a 10 ml. sample into each of two 250 ml. Erlenmeyer flasks and dilute to approximately 150 ml. with distilled water. Mark the two flasks 1 & 2.

(1) Chromic acid determination

To the Erlenmeyer flask marked #1 add 2 g. ammonium bifluoride to eliminate the effect of the iron present in the solution. Add 15 ml. concentrated HCl. Then add 10 ml. potassium iodide solution (100 g/liter KI and 1 g/liter KOH). Titrate the liberated iodine with 0.1 N $Na_2S_2O_3$ until the green color of the chromate predominates over the brownish-red free iodine color. Add 5 ml. prepare starch solution and continue the titration until the blue color of the starch solution is just destroyed. Care must be taken not to confuse the green color of the chromate with the blue color of the starch. Record the volume of $Na_2S_2O_3$ required for the titration.

The amount of chromium present may be calculated from:

1 ml. 0.1 N $Na_2S_2O_3$ = 0.001734 g. chromium

(2) Total chromium determination.

To the Erlenmeyer flask marked #2 add 0.2 g. sodium peroxide and boil the solution for 20-30 minutes. Dilute to 150 ml. with

distilled water and allow to cool. From this point continue as in the procedure given in the preceding section #1, Chromic Acid Determination. The total amount of chromium present is calculated from:

$$1 \text{ ml. } 0.1 \text{ N } Na_2S_2O_3 = 0.001734 \text{ g. Cr.}$$

DETERMINATION OF SUSPENDED SOLIDS IN CLEANING SOLUTIONS

Take sample from these tanks in such a way as to get a representative sample. If necessary tie a wire onto the bottle stopper and when the bottle is near the bottom of tank remove the stopper by pulling the wire.

Clean and number the Gooch crucibles. Dry in oven for at least one hour at 120° C. Cool in desiccator and weigh.

Pour 250 ml. of sample through Gooch, using suction. Wash 4 or 5 times with distilled water, completely filling crucible with water each time. Dry in oven for 1 hour at 120° C. Cool in desiccator and weigh. The gain in weight in milligrams X 4 will be milligrams per liter. Record as such on the Laboratory Report Sheet.

<u>HYDROCHLORIC ACID — TANK CAR</u>

Specific gravity:

Take the gravity of the acid with a hydrometer graduated in oil degrees Bé, the acid being at a temperature of 60° F. when the reading is made. Convert Sp. Gr. to % HCl. (Lange's Handbook, 1117-1118).

Total Acidity:

Weigh 2 ml. of the acid into a tared weighing bottle, then add a few drops of distilled water and mix. Transfer to beaker and add methyl orange indicator. Titrate to a yellow end point with 0.5 N NaOH.

Calculation:

$$\frac{(ml.)\ (N)\ (0.03646)}{Wt.\ sample} = \%\ HCl$$

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ANALYSIS OF L-28 FOR O$_2$

Sampling Procedure

Take Dewar flask to building A-1408 to have filled with L-28 from storage tank. Braing sample to furnace area to be analyzed.

Note: Make sure O$_2$ gas analysis apparatus is calibrated from the zero on the burette to the two way stopcock on the left leading into the potassium pyrogallate solution.

First remove male joint from Orsat apparatus and replace with a short piece of rubber tubing. Fill Orsat with water to the left stopcock to remove all gas from apparatus.

Next see that no stopcock lube (2144) is on the stopcocks and that the bulb is perfectly dry.

Immerse bulb in L-28 with the stopcocks open and the upper stopcock (the one next to the female joint) just out of the L-28 to keep it from getting too cold to handle. Close stopcock and lift bulb out with sample.

The pressure of the L-28 will force out all other gases present. Attach bulb to rubber tube and open stopcock to let sample into the burette.

While sample is warming up to room temperature take a barometer reading and record data.

When sample is at room temperature take first reading and record data. Absorb O$_2$ from gas by passing through potassium pyrogallate solution and then measure residual gas.

Note: If volume increases remove sample and repeat procedure allowing a longer period of time for the gas to warm up. When a constant reading is obtained you may record data.

<u>Calculation of O_2 in L-28:</u>

Barometer reading minus temperature of water, divide difference by barometer reading. This will give the vapor correction factor which we call (X).

V_1 = Volume gas at beginning plus ml. from 0 to stopcock.

V_2 = Volume gas after O_2 is absorbed plus ml. from 0 to stopcock.

$$X \times V_1 = V_1X$$

$$X \times V_2 = V_2X$$

(1) $V_1X - V_2X$ = Volume O_2

(2) $\dfrac{(Vol.\ O_2)(14.5)}{(V_1X)\ (14.7)} \times 100 = \%\ O_2$ in L-28

PROCEDURE FOR CHROMIUM DETERMINATION

Water Samples

Procedure:

Filter sample, using #1 or #41 H filter paper. Measure out 100 ml. of filtered samples into a 400 cc beaker. Add 2 grams sodium peroxide, Na_2O_2. Dilute to 200 ml. volume and boil to one-fourth volume (50 cc). Remove from hot-plate and dilute to 150 ml. with distilled water. Add 20 ml. 85% phosphoric acid and boil for 15 minutes.

While hot, add drop by drop enough 0.02 N $KMnO_4$ solution to give a distinct pink tint that lasts for one minute.

Cool in ice bath. Add 5 ml. 0.04 N ferrous ammonium sulfate solution. Let stand 5 minutes and titrate against the 0.02 N $KMnO_4$ solution to pink tint.

Blank:

To 100 ml. distilled water add 10 ml. phosphoric acid and titrate drop by drop with $KMnO_4$ to very faint pink. Add 5 ml. 0.04 N ferrous ammonium sulfate solution and titrate against $KMnO_4$ solution.

Calculation:

$$(\text{Blank} - \text{ml. } KMnO_4)(\text{Normality of } KMnO_4)(0.01734)(10) = \text{grams/liter of Chromium.}$$

PROCEDURE FOR DETERMINING SAPONIFICATION NUMBER ON OILS

Weigh accurately, by difference, 2 to 3 grams of the material into the saponification flask. Measure accurately into the flask with a calibrated pipet 25 ml. of alcoholic KOH solution. Then add 50 ml. of ethyl alcohol (99.95% pure), rinsing out pipet. Connect the flask to a suitable condenser and boil for three hours. Before disconnecting, wash down the sides of the condenser with a little ethyl alcohol. Titrate while hot with 0.5 N HCl using phenolphthalein as an indicator. A blank determination should be run on the reagents, using exactly the same procedure except, of course, omitting the addition of the sample.

Calculations:

The saponification number equals the difference between the number of milliliters of 0.5 N HCl required for the determination and the blank, using the formula:

$$\text{Saponification number} = \frac{(\text{ml. difference of HCl}) (28.05)}{\text{weight of oil in grams}}$$

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ACID NUMBER OF OILS

Weigh accurately about 10 g. sample of oil in an Erlenmeyer flask. Add 50 ml. of ethyl alcohol (previously titrated to a faint pink with NaOH using phenolphthalein as an indicator). Shake well and heat to boiling. Titrate while still hot with 0.1N NaOH to phenolphthalein end-point.

Calculations:

$$\frac{(ml.\ NaOH)(mg.\ NaOH\ in\ 1.0\ ml.)}{Weight\ of\ Oil} = mg.\ NaOH/g.\ oil$$

Scott's Standard Methods of Chemical Analysis: Vol. II, pp. 1818-1819.

IODINE NUMBER OF OILS

Weigh an empty 500 ml. iodine flask. Add approximately 0.1 to 0.2 gram sample of oil. Weigh flask again. Add 10 ml. of chloroform. Whirl flask until sample has dissolved. Add 30 ml. of iodine solution and let sample stand for one hour shaking sample occasionally. Add 10 ml. of 15% KI and dilute with 100 ml. of distilled water, washing down the sides of the flask. Titrate with 0.1 N sodium thiosulfate solution using starch solution as indicator. A blank should be run with each sample, using the same procedure.

Calculations:

$$\frac{(\text{ml. } Na_2S_2O_3 \text{ for blank} - \text{ml. } Na_2S_2O_3 \text{ for sample})(\text{mg. } Na_2S_2O_3/\text{ml.})}{\text{Wt. of Oil}} = \text{mg. } I_2/\text{g. of oil.}$$

Scott's Standard Methods of Chemical Analysis:

Vol. II, pp. 1767.

PROCEDURE FOR CLEANING ION GAUGE TUBES

Solutions:

A - 10% sodium carbonate or 15% Soda Ash.

B - 1 volume reagent grade ammonium hydroxide to 4 volumes water.
Keep new solutions ready to replace dirty ones.

Procedure:

Number each half of ion gauge tube so that mixing will not occur. The glassblower must have matching parts in order to reassemble them properly.

Heat solution A to 200°F. and immerse filament part of tube in it. Keep in solution for 30 minutes or until the oxide coating comes off. Rinse filament with distilled water.

Heat solution B to 160°F. and immerse shell of tube in it for 4 minutes. Then dip shell in beaker of water and rinse carefully. (Do not subject the platinum coating or shell to violent currents such as result from washing in a running stream of water). If the platinum is still slightly cloudy it may often be cleaned by wiping with a cheesecloth when it is dry. Dry both parts with alcohol and acetone.

PREPARATION OF VOLUMETRIC STANDARD SOLUTIONS

1. Sodium Hydroxide (0.1N)

Weigh out about 470 grams of analytical reagent grade NaOH (pellet) on trip balance, dissolve in 400 ml. of distilled water, and allow to settle for several weeks. Measure 5 ml. of the concentrated solution in a graduated cylinder and dilute to 1 liter with distilled water. (Any amount of solution may be prepared in this way).

Standardization: Dry about 10 grams of primary standard analytical reagent grade potassium acid phthalate in an oven for at least two hours. Weigh accurately three 0.5106 gram portions of the potassium acid phthalate on an analytical balance. Treat each portion in the following manner: Dissolve the potassium acid phthalate in about 50 ml. of CO_2 free water in a 250 ml. Erlenmeyer flask. Add 3 drops of phenolphthalein indicator and titrate to a pink color with the 0.1 N NaOH.

(0.5106 gram potassium acid phthalate is equivalent to 25 ml. 0.1000 N NaOH).

Calculation: $N \text{ NaOH} = \dfrac{\text{grams potassium acid phthalate}}{(\text{ml. NaOH}) \ (0.204)}$

Calculate the amount of water to be added to the solution to make exactly 0.100 N NaOH by the following formula.

$$V = \frac{(1000) \ (N^1 - N)}{N}$$

Where N = the desired normality

N¹ = the normality found

V = ml. of water per liter of the solution required to dilute it to the desired normality. Add the amount of water calculated and repeat the standardization.

2. Hydrochloric Acid (0.1N)

From a graduated cylinder carefully add 152 ml. of concentrated analytical reagent grade HCl to 18 liters of distilled water contained in a five gallon bottle. Mix thoroughly.

Standardization: From a burette measure 30-35 ml. of the diluted acid into a 250 ml. Erlenmeyer flask and wash down the sides of the flask with about 75 ml. of distilled water. Add 2-3 drops of phenolphthalein indicator and titrate with standard 0.1 N sodium hydroxide to the first permanent pink end point.

$$N \text{ HCl} = \frac{(N \text{ NaOH}) \ (ml. \text{ NaOH})}{(ml. \text{ HCl})}$$

Calculate the amount of water to be added to the solution to make exactly 0.100 N HCl by the following formula:

$$V = \frac{(1000)}{N}(N^1 - N)$$

Where N = the desired normality

N^1 = the normality found

V = the ml. of water per liter of the solution required to dilute it to the desired normality. Add the amount of water calculated and repeat the standardization.

3. Potassium Dichromate (0.100 N)

Dry about 10 grams of finely ground analytical reagent grade $K_2Cr_2O_7$ in an oven at 110° C. for at least two hours. Weigh out 4.903 grams of the dried salt, dissolve in distilled water and dilute in a volumetric flask to one liter with distilled water. This solution will be exactly 0.100 N.

A. Sodium Thiosulfate (0.1 or 0.2N)

1. Weigh out 450 grams $Na_2S_2O_3 \cdot 5H_2O$ for 18 liters of 0.1 N solution.

2. Weigh out 900 grams $Na_2S_2O_3 \cdot 5H_2O$ for 18 liters of 0.2 N solution.

3. Dissolve the $Na_2S_2O_3 \cdot 5H_2O$ by agitation in about 1000 ml. of water in a large beaker. When dissolved, add about 0.10 grams Na_2CO_3 to preserve the solution, transfer to the 18 liter carboy and add distilled water to the 17.5 liter mark.

Standardization: Dissolve 2-3 grams of KI in 200 ml. of distilled water and add 10 ml. of 1:1 HCl. Measure accurately, from a burette into a glass stoppered flask containing the KI solution, 30-40 ml. of 0.100 N potassium dichromate, and allow to stand for a period of 5-10 minutes. Titrate with the $Na_2S_2O_3$ solution until the solution is light yellow. Add 2-3 ml. of starch indicator and titrate to the disappearance of the blue starch color. (A slight green color will remain).

Calculation: $N\ Na_2S_2O_3 = \dfrac{(ml.\ K_2Cr_2O_7)\ (0.100)}{Ml.\ Na_2S_2O_3}$

Calculate the amount of water to be added to the solution to make exactly the required normality by the following formula:

$$V = \frac{(1000\ (N^1 - N)}{N}$$

Where N = the desired normality

N^1 = the normality found

V = ml. of water per liter of the solution required to dilute it to the desired normality. Add the amount of water calculated and repeat the standardization.

5. Ceric Ammonium Sulfate (0.05N)

Weigh out two 300 gram portions of ceric ammonium sulfate and put each in a 4 liter beaker. Add 500 ml. of concentrated sulfuric acid to each beaker.

VERY SLOWLY add 500 ml. of water to each beaker WITH CONSTANT STIRRING. Add four more 500 ml. portions of water to each beaker, being careful to avoid spattering. The total volume in each beaker will now be 3 liters.

In an 18 liter carboy measure 10 liters of distilled water and add the contents of each beaker to the carboy. Rinse each beaker with one liter of distilled water and bring the volume in the carboy to 18 liters. Mix the contents of the carboy thoroughly.

6. Ceric Ammonium Sulfate (0.01 N)

Carefully measure 200 ml. of the 0.05 N ceric ammonium sulfate solution into a 1 liter volumetric flask. Add 45 ml. of concentrated sulfuric acid and dilute to the mark with distilled water.

7. Ferrous Ammonium Sulfate (0.05 N)

Weigh out 180 grams of $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ and put in a 4 liter beaker. Add 2.5 liters of distilled water and then slowly with stirring add 500 ml. of concentrated sulfuric acid.

Measure 5 liters of distilled water into a 9 liter carboy and add the 3 liters of solution to it. Rinse out the beaker with distilled water to make volume up to 9 liters. Mix thoroughly.

8. Ferrous Ammonium Sulfate (0.01 N)

Dilute 200 ml. of the above 0.05 N ferrous ammonium sulfate to 1 liter with distilled water.

9. __Starch Solution__

Mix 5 grams of soluble starch thoroughly with a little distilled water. Pour with constant stirring into 500 ml. of boiling water. Allow the solution to cool and add 10 grams of KI.

10. __Phenolphthalein Indicator__

Dissolve 1 gram of phenolphthalein in 50 ml. of 95 per cent alcohol and add 50 ml. of distilled water. Add 0.1 N NaOH slowly until the solution __almost__ changes to pink (i.e. so the next drop would make the indicator change).

PHOTOGRAPHIC SOLUTIONS

DEVELOPER D-19

1. Assemble the following materials needed: hot plate, 4 liter beaker, stirring rod, thermometer, scales, spatula, funnel, labels, four one liter bottles, and 1000 ml. graduate.

2. Heat 2 liters of distilled water to 50° C. and remove from hot plate.

3. Add chemicals in the order given, taking care that each is dissolved before adding the next:

Elon...	8.8 grams
Sodium sulfite, desiccated...................	384.0 grams
Hydroquinone.................................	35.2 grams
Sodium carbonate, desiccated.................	192.0 grams
Potassium bromide............................	20.0 grams
Cold distilled water to make.................	4.0 liters

4. Pour solution in bottles and label.

5. Place in refrigerator until ready for use.

DEVELOPER DK-50

1. Assemble the following materials needed: hot plate, liter beaker, stirring rod, thermometer, scales, spatula, funnels, labels, liter bottle, and 1000 ml. graduate.

2. Heat 500 ml. of distilled water to 50° C. and remove from hot plate.

3. Add chemicals in the order given, taking care that each is dissolved before adding the next:

Elon..2.5 grams

Sodium sulfite, desiccated..................30.0 grams

Hydroquinone................................2.5 grams

Kodalk......................................10.0 grams

Potassium Bromide...........................0.5 grams

Cold distilled water to make................1.0 liters

4. Pour solution in bottle and label.

5. Place in refrigerator until ready for use.

DEVELOPER D-72

1. Assemble the following materials needed: hot plate, 4 liter beaker, stirring rod, thermometer, scales, spatula, funnels, labels, four one liter bottles, and 1000 ml. graduate.

2. Heat 2 liters of distilled water to 50° C. and remove from hot plate.

3. Add chemicals in the order given, taking care that each is dissolved before adding the next:

Elon..12.4 grams

Sodium sulfite, desiccated..................180.0 grams

Hydroquinone................................48.0 grams

Sodium carbonate............................270.0 grams

Potassium bromide...........................7.6 grams

Cold distilled water to make................4.0 liters

4. Pour solution in bottles and label.

5. Place in refrigerator until ready for use.

DEVELOPER D-8 (MODIFIED)

1. Assemble the following materials needed: hot plate, liter beaker, stirring rod, thermometer, scales, spatula, funnels, labels, liter bottle, and 1000 ml. graduate.

2. Heat 500 ml. of distilled water to 50° C. and remove from hot plate.

3. Add chemicals in the order given, taking care that each is dissolved before adding the next:

Sodium sulfite, desiccated......................60.0 grams

Hydroquinone......................................30.0 grams

Sodium hydroxide..................................20.0 grams

Potassium bromide.................................30.0 grams

Cold distilled water to make.....................1.0 liters

4. Pour solution in bottle and label.

5. Place in refrigerator until ready for use.

FIXING BATH F-1

Solution A

Distilled water............................3 liters

Sodium thiosulphate........................720 grams

Solution B

Water at about   ° C.......................240 ml.

Sodium sulphite, desiccated................45 grams

Acetic acid (28%)..........................129 ml.

Potassium alum.............................45 grams

(To make 28 per cent acetic acid - dissolve 36 ml. of glacial acetic acid in 93 ml. of distilled water.) Add each ingredient in the order of listing. Be sure that each is thoroughly dissolved before adding the next one. After solution B has cooled, add to solution A.

FIXING BATH F-5

1. Assemble the following materials: hot plate, 1-2 liter beaker, stirring rod, thermometer, scales, funnel, labels, one liter bottle, 1000 ml. graduate.

2. Heat 600 ml. of distilled water to 50° C.

3. Dissolve the following chemicals in the order given, taking care that each chemical is dissolved before adding the next:

Sodium thiosulfate................................240.0 grams

Sodium sulfite, desiccated........................15.0 grams

Acetic acid (Glacial).............................13.2 ml.

Boric acid (crystals).............................7.5 grams

Potassium alum....................................15.0 grams

Cold distilled water to make......................1.0 liter

4. Pour solution in bottle and label.

5. Place in refrigerator.

SPECIAL SPECTROGRAPHIC FIXING BATH

1. Assemble the following materials: hot plate, 1-2 liter beaker, stirring rod, thermometer, scales, filter paper, funnel, labels, one liter bottle, 1000 ml. graduate, and 100 ml. graduate.

2. Heat 600 ml. of distilled water to 50° C.

3. Dissolve the following chemicals in the order given, taking care that each chemical is dissolved before adding the next:

> Sodium thiosulfate...........................300.0 grams
>
> Ammonium chloride............................60.0 grams
>
> Sodium bisulfite.............................45.0 grams
>
> Cold distilled water to make.................1.0 liter

4. Pour solution in bottle and label.

5. Place in refrigerator.

ACID RINSE BATH

1. Assemble the following materials: bottle, funnel, label, 100 ml. graduate.

2. Put 18.0 ml. of glacial acetic acid in bottle and fill with one liter of distilled water.

3. Label and put solution in the refrigerator.

PREPARATION OF SOLUTIONS

Reference: Scott, Standard Methods of Chemical Analysis

I. Indicators

A. Methyl Red

Dissolve 0.5 g. of the powder in 300 ml. of alcohol and make up to 500 ml. with distilled water in a volumetric flask. End-point = pH 5 pH range = 4.4 - 6.2

B. Methyl Orange.

Dissolve 0.5 g. of the powder in 500 ml. of distilled water in a 500 ml. volumetric flask. End-point = pH 4 pH range = 3.1 - 4.4

C. Phenolphthalein

Dissolve 1.0 g. in 100 ml. of 95% alcohol. If 1 or 2 drops of this solution are used per 100 ml. of solution titrated, the end-point is at pH 9.

D. Starch Indicator.

Make 5 g. potato starch or arrowroot starch into paste with cold water and pour the paste into 2 liters of boiling distilled water. The solution. is kept in a glass-stoppered bottle.

II. Standard Solutions

In the preparation of standard solutions, only analytical reagent grade chemicals should be used.

A. Sodium Hydroxide (0.5 N)

1. Preparation

Dissolve 400 g. of analytical reagent grade hydroxide in

400 ml. distilled water and allow to stand for at least 24 hours.
Withdraw supernatant liquid and use for the preparation of the
standard solution. Make sure that there is no sediment present.
For a 1 N solution there should be 40.005 g. 100% NaOH per liter.

2. Standardization

(a) With constant boiling HCl. Set up a distilling appa-
ratus with a liter flask and water condenser. Place about
750 ml. of analytical reagent grade HCl diluted at 22-23%
HCl in the flask and distill. After the solution becomes
constant boiling (i.e., boils without deviation in the temp-
erature) allow the first quarter of the solution distilled
to be discarded. Collect the next half of the solution dis-
tilled in a clean, dry flask and discard the remainder of the
solution in the distilling flask. Record one barometer read-
ing (read to the nearest mm.). Store acid in a glass-stop-
pered bottle.

As a further check on the acid weigh 2 ml. of the acid
in a tared weighing bottle and transfer to a clean beaker.
Dilute to 100 ml. and add 2 ml. dilute nitric acid and heat.
Add hot silver nitrate in slight excess to that required to
precipitate the HCl, as calculated from the weight of acid
in each ml. of the sample. For this purpose use a silver
nitrate solution containing 4.8 g. $AgNO_3$ per 100 ml. of
distilled water. This solution will precipitate 0.01 g.
chlorine or 0.0404 g. AgCl. When the precipitation of

the AgCl is complete, prepare a Gooch crucible filter with a moderately thick asbestos mat. Dry and weigh. Filter the precipitate after washing first by decantation and then washing free of chloride with water containing HNO_3. Dry and weigh to determine the weight of AgCl present. The weight of HCl may be calculated from (AgCl) (0.2544) = HCl. The percentage of HCl is compared to the percentage determined for the constant-boiling mixture.

To use for standardizing 0.5 NaOH, weigh 2 ml. sample of the acid in a clean, dry tared weighing bottle and transfer to a beaker. Dilute to 150 ml. and add 2 drops methyl orange indicator. Titrate with the unknown alkali to the orange-yellow end-point. Standardize the NaOH solution also by using methyl red and phenolphthalein indicators. The strength of the alkali is calculated from:

$$\frac{(Wt. \ of \ HCl \ in \ Sample)}{(Ml. \ of \ NaOH \ used)} \frac{(1)}{(0.03647)} = Normality \ of \ NaOH$$

If the solution is not 0.5 N, the necessary amount of alkali or water should be added to produce that strength. (Note: Duplicate samples should be used in each determination in the procedure.)

(b) With potassium acid phthalate. Weigh 2-5 g. of the salt and dissolve in 100 ml. distilled water. Using phenolphthalein indicator titrate with the 0.5 N NaOH solution to the pink end-point. (When the end-point is reached heat the solution to boiling; if color fades, add more of the

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NaOH solution until the pink color persists for 30 seconds
after boiling.)

Compute the normality of the NaOH from:

$$\frac{(\text{Wt. potassium acid phthalate})}{(\text{Ml. of NaOH used})} \frac{(1)}{(0.2042)} = \text{Normality of NaOH}$$

Adjust the normality if necessary and recheck by this
method.

(Note: Duplicate samples should be used in each determina-
tion.)

B. Hydrochloric Acid   (0.5 N)

1. Preparation.

Place 43 ml. analytical reagent grade HCl (sp. g. 1.19 =
36% HCl) in a 1000 ml. volumetric flask; dilute to mark with
distilled water and mix thoroughly.

2. Standardization.

Prepare pure sodium carbonate by dissolving 35 g. of impure
reagent in 350 ml. of warm water and filter to remove any insol-
uble residue. Allow the water to evaporate slowly at a tempera-
ture not above 40°C. until about 25 g. of the sodium carbonate
has been deposited. Pour off the mother liquor and dry the cry-
stals for an hour at 120°C. Place about 8 g. of the salt in a
porcelain crucible and heat for 30 minutes at 270°C. Store dry
salt in a glass-stoppered bottle.

To standardize 0.5 N HCl weigh out a sample of 1 g. of the
Na_2CO_3 in a glass-stoppered weighing bottle. Dissolve in dis-
tilled water and transfer to a beaker, being careful to avoid any

loss of the solution. Add methyl orange indicator and titrate to end-point with the acid being standardized. The normality of the acid is:

$$\frac{(Wt. \ Na_2CO_3)}{(Ml. \ HCl \ used)} \ \frac{(1)}{(0.0530)} = \ Normality \ of \ HCl$$

If the acid is not 0.5 N an adjustment may be made by adding either acid or distilled water. The acid should then be rechecked by this method.

(Note: Duplicate samples should be used in this determination.)

C. Potassium Permangante (0.1 N)

1. Preparation.

Dissolve 3.3 g. of $KMnO_4$ in a liter of distilled water. Mix well and allow to stand for several days. Filter solution through glass wool into the storage bottle (preferably a dark bottle).

(Note: Permanganate solution should not come in contact with rubber, filter paper, or other organic materials.)

2. Standardization.

Use Bureau of Standards sodium oxalate. Dry the sodium oxalate at 105°C immediately before use. Dissolve 0.25 to 0.30 g. of sodium oxalate in 200 ml. of hot water (80-90°C) in a clean beaker and add 10 ml. of 1:1 sulfuric acid. Titrate it immediately with the permanganate solution, stirring or shaking vigorously and continuously. The permanganate must not be added more rapidly than 10-15 mls. per minute. Allow each drop of permanganate to be completely decolorized before adding the next drop when near the end-point. Run a blank to determine the volume of permanganate required to produce the same color in

-6-

the same volume of water and acid.

(Note: The temperature of the solution at the end-point should not be below 60°C.)

The normality of the solution is calculated as follows:

$$\frac{(\text{Wt. of sodium oxalate})}{(\text{Net ml. permanganate used})} \left(\frac{1}{0.0670}\right) = \text{Normality of KMnO}_4$$

D. Sodium thiosulfate (0.1 N)

1. Preparation.

Dissolve 25 g. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ per liter of distilled water.

If any sulfur has settled out, decant the clear liquid and filter if necessary.

2. Standardization.

Standardize the sodium thiosulfate solution by titration with a prepared standard iodine solution - see F (Iodine solution 0.1 N). The normality of the thiosulfate solution is calculated as follows:

$$\frac{(\text{Ml. Iodine used})(\text{N. of Iodine Solution})}{\text{Ml. Na}_2\text{S}_2\text{O}_3 \text{ used}} = \text{Normality of Na}_2\text{S}_2\text{O}_3$$

The strength of the thiosulfate solution should be checked frequently.

E. Ferrous Sulfate (0.1 N)

1. Preparation.

Dissolve 39.5 g. $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ in 50 ml. 6 N H_2SO_4 and dilute to one liter with distilled water.

2. Standardization.

Standardize the solution by titration with a prepared standard KMnO_4 solution (see C-Potassium permanganate 0.1 N). The normality

of the ferrous sulfate is calculated as follows:

$$\frac{(\text{Mls. KMnO}_4 \text{ used}) (\text{N KMnO}_4)}{\text{Mls. Ferrous Sulfate}} = \text{Normality of FeSO}_4$$

F. Iodine Solution (0.1 N)

  1. Preparation

    Dissolve 12.7 g. resublimed iodine and 20 g. pure potassium iodide in 50 ml. water. After the iodine is completely dissolved, transfer the solution to a glass-stoppered liter flask and dilute with pure distilled water to the mark. Mix well and stopper the bottle.

  2. Standardization.

    Use Bureau of Standards As_2O_3 for the standardization.

    The As_2O_3 solution is prepared by weighing 4.95 g. of arsenious oxide in a weighing bottle. (The tare of the bottle is taken after the arsenious oxide is removed.) Transfer the As_2O_3 to a liter flask, moisten, add 15 g. of pure NaOH and 100 ml. of distilled water. Mix gently until the arsenious oxide is dissolved. Dilute to the mark and mix thoroughly.

    To standardize the iodine solution, transfer an accurately measured 40-50 ml. portion of the arsenious oxide to a flask and titrate with the iodine solution, using starch indicator. In order to obtain accurate results it is necessary that the solution be saturated with carbon dioxide at the end of the titration. To effect this saturation a few drops of HCl may be added near the end-point to liberate sufficient carbon dioxide to saturate the solution. Titrate to the pink

or rose-colored end-point. The normality of the solution is calcu-

lated as follows:

$$\frac{(\text{ Wt. of } As_2O_3 \text{ in Sample })}{(\text{ Mls. Iodine solution used})} \quad \frac{(\quad 1 \quad)}{(0.049455)} = \text{Normality of Iodine Solution}$$

PROCEDURE FOR CLEANING FILAMENTS

Make a solution of 1 part nitric to 3 parts hydrochloric acid and pour in pyrex tray. Place tray of filaments over the solution so that the tips of the filaments will be immersed in the solution. Put tray on hot-plate and heat (60°C to 80°C.) for at least 30 minutes. Remove and wash each filament with water. If the tips of the filaments are not clean and smooth, let stand in acid solution for a few more minutes and wash again with water.

PROCEDURE FOR CLEANING RUBBER GASKETS

1. Wash in soap solution (Lux or Ivory flakes). A true solution of soap should be used, and the presence of undissolved soap particles which might adhere to the rubber parts must be avoided.

2. Thoroughly rinse in clean water.

3. Immerse in 2% sodium hydroxide solution at 150°F. for 15 minutes.

4. Rinse thoroughly in warm (120°F.) water.

5. Hang over steel rods to dry.

6. Wrap in paper.

Note: Do not touch gaskets with bare hands after they have been washed. Use tongs or rubber gloves when handling them.

PROCEDURE FOR REDISTILLING WATER

Set up distilling apparatus using a 5000 ml. distilling flask. Add about 2 grams potassium permanganate and about 1 gram of calcium hydroxide (barium oxide or lime may be used) to flask and fill with distilled water. Apply heat by means of a Bunsen burner and catch distillate in beaker.

CAUSTIC SCRUBBER

Building #1301

To Determine Percent KOH or NaOH

Pipet a 5 ml sample into a 250 ml. Erlenmeyer flask and dilute with distilled water to 100 ml. Add 2 drops phenolphthalein indicator. The solution will be pink. Titrate with 0.5 N HCl to the end-point (the solution will turn colorless upon the addition of one drop of HCl). Record mls. HCl used on report sheet. Make final report (using graph #1301).

MISCELLANEOUS

I. DISTILLATION OF METHYL METHACRYLATE MONOMER

1. Grease all ground glass joints.

2. Around the receiving flask place a crystallizing dish containing powdered dry ice and trichlorethylene.

3. Fill distilling flask with 250-350 ml. of methyl methacrylate monomer.

4. Apply vacuum, be sure that the liquid does not boil too vigorously and cause "carry-over" to the receiving flask.

5. After four or five minutes, apply a little heat to the distilling flask. Be careful that the liquid does not boil too vigorously.

6.. The distillation is continued until there are about 10-15 ml. of liquid remaining in the distilling flask. This residue is to be thrown away.

7.. Before storing the apparatus, clean thoroughly, making sure that all ground glass joints have been cleaned with an organic solvent.

II. PREPARATION OF "KOROSORB" TUBES

1. Dissolve 2.5 grams Congo Red ("Certified" Eastman Kodak or Paragon Testing Laboratories) in a mixture of 500 ml. distilled water and 500 ml. of 95 per cent ethyl alcohol.

2. Place 150 grams of soda lime granules in a clean beaker. ("Wilson's" Sodium - Calcium Hydrate, 2 per cent moisture, 14-20 mesh granules obtained from Eimer and Amend (or equivalent is used.) Add a volume of congo red solution which is just sufficient to wet the soda lime. Stir the mixture with a glass rod until all the granules are colored red.

3.   Transfer the wet, colored granules to several layers of large absorbent filter paper and spread these on a flat pan or plates. Place the pan in a drying oven and dry at 80° C. Store the Korosorb in well-stoppered bottles.

4.   Insert a 1/8 in. glass wool plug against the constriction of the Korosorb tube. Place three grams Korosorb in the tube and tap the constricted end of the tube gently against a clean surface until the Korosorb is firmly packed. Then insert another 1/8 in. glass wool plug in the tube to hold the granules in place. The length of absorbent column will be 7 cm.

III.   PREPARATION OF "SALAC" TUBES

A.   Six inch tube

1.   Place a 1/8 in. plug of glass wool at the constricted end of the tube.

2.   Weigh out 1.5 grams of salicylic acid and place in the tube so that it fills 1-1/4 in. of the tube. (A plunger may be used for packing the material in the tube so that it has the desired length.)

3.   Place 1/8 in. plug of glass wool over the salicylic acid.

4.   Store in a desiccator.

B.   Five inch tube

Follow the above directions except use 0.6 grams of salicylic acid and pack to a depth of 3/4 inches.

DETERMINATION OF T IN T_3O_8 SAMPLES

Method:

This method consists essentially in treating the oxide samples to remove ions which interfere with the ceric sulfate procedure for determining T. Volatile interfering ions such as fluoride and nitrate are removed by fuming the sample to dryness twice with sulfuric acid. Metallic interfering ions such as iron and copper are removed by electrolyzing the dissolved sample in a mercury cathode cell apparatus. (See Procedure 7.3). The isolated T can then be reduced and titrated with ceric ammonium sulfate solution.

Reagents and Apparatus:

1. Concentrated hydrochloric acid.

2. Concentrated nitric acid.

3. Concentrated sulfuric acid.

4. Dilute sulfuric acid (3 N) and (6 N).

5. Standard ceric ammonium sulfate solution - Dissolve sufficient ceric ammonium sulfate in 2 N sulfuric acid to give a ceric concentration of 0.05 N. The solution should stand about two weeks and be filtered before standardizing.

6. Ferrous ammonium sulfate solution - Dissolve sufficient ferrous ammonium sulfate in 2 N sulfuric acid to give a ferrous concentration of 0.05 N.

7. Ortho phenanthroline indicator - Dissolve sufficient ortho phenanthroline in 0.025 M ferrous sulfate to make the resulting solution 0.075 M with respect to the ortho phenanthroline indicator.

8. Jones reductor - Prepare as in Procedure 7.1.

9. Mercury cathode apparatus - See Procedure 7.3.

Procedure:

A. Sample Preparation and Sample Solution:

1. Thoroughly grind and mix about one gram of the sample in an agate mortar. (Recover material adhering to the mortar by dissolving it in concentrated sulfuric acid; rinse with water and save washings. All T_3O_8 material must be salvaged.)

2. Weigh 0.2 gram samples into 400 ml. beakers.

3. Add a sufficient amount of concentrated hydrochloric acid to cover the sample and bottom of beaker. Heat until small bubbles cease, but do not allow sample to go to dryness.

4. Add 10 ml. of concentrated nitric acid and heat until sample dissolves. Some samples do not go completely into solution with nitric acid but if the color of the residue is different from that of the original sample, continue with procedure as if solution were complete.

5. Add 2 ml. of concentrated sulfuric acid and evaporate to dryness. Dissolve the sample in 6 N sulfuric acid and evaporate to dryness again.

Purification of Sample:

1. Dissolve sample from Step 5, Part A above in sulfuric acid using enough acid to give a total volume of 75 ml. Heat on a hot plate until solution is complete.

2. Transfer the sample to a water-jacketed mercury cathode cell and electrolyze with stirring at 3.0-3.5 amperes for one hour. Use 2 N sulfuric acid as a rinse when transferring the sample from the beaker to the cell to maintain the proper acidity. Keep the volume of the

sample at 75-100 ml. (Note: Mercury may be used three times in the cell before being redistilled. Triple-distilled mercury is best.)

3. Remove from cathode and filter immediately through Watman No. 2 filter paper. Wash paper thoroughly with water.

4. Place sample on hot plate and reduce volume to about 100 ml.

Reduction of T:

1. Clean and activate the Jones reductor by passing 300 ml. of 2 N sulfuric acid through it. Add about 200 ml. of water to displace the acid in the reductor.

2. Carry out a "blank" titration as follows: Pass 150 ml. of 2 N sulfuric acid through the reductor followed by 200 ml. of water.

3. Determine the "blank" by adding 25-30 ml. of standard ceric ammonium sulfate, 2 drops of ortho phenanthroline complex and titrating to a salmon pink end-point with ferrous ammonium sulfate solution.

4. Carry out a cross-titration as follows: Titrate 25-30 ml. of ceric ammonium sulfate solution in 150 ml. of 1 M sulfuric acid with the ferrous ammonium sulfate solution using 2 drops of ortho phenanthroline complex as before.

5. Calculate the cross-titer values obtained in (3) and (4) by dividing the volume of ceric ammonium sulfate used by the volume of ferrous ammonium sulfate and compare the values obtained. If the cross-titers do not check within 2 parts in 1000 repeat steps (3) and/or (4).

6. Reduce the sample as before. Pass 50 ml. of 2 M sulfuric acid through the reductor. Then pass the entire sample containing T through the reductor.

-4-

Wash the beaker with two 25 ml. portions of acid and pour the washings through
the reductor. Wash the beaker with water and run the washings through the re-
ductor. Add sufficient water to bring the total wash water to 100-150 ml.
Aerate the sample for at least five minutes to convert trivalent T (olive
green) to the quadrivalent state.

Titration:

1. Add 3 drops of ortho phenanthroline complex to the sample. Add
    ceric ammonium sulfate until the color changes and then add about
    1-2 ml. excess.

2. Back-titrate to a salmon pink end-point with ferrous ammonium sul-
    fate solution.

Calculations:

$$\frac{(A - B \times cross\ titer) \times Me \times N}{W} \times 100 = percent\ T\ in\ sample$$

A = ml. of ceric ammonium sulfate used.

B = ml. of ferrous ammonium sulfate used.

Me = milliequivalent weight of T (0.119).

N = normality of ceric ammonium solution.

W = weight of sample.

% T X 1.179 = % T_3O_8

Note: This method does not take care of all possible interfering substances.
It has however been applied successfully to comparatively high grade "black
oxide" samples containing small amounts of common impurities such as iron,
nitrate, etc.

DETERMINATION OF T USING SODIUM PEROXIDE

Method:

This is a rapid method, suitable for control work, for determining hexavalent T in quantities up to 100 mg. Five per cent sodium peroxide solution reacts with T to give an intensely yellow pertuballate. The transmission at 410 mu is measured with the Cenco Photelometer or other photelectric colorimeter and the amount of T in solution is obtained from this value by means of a calibration curve.

Reagents:

1. Sodium peroxide solution, 5 per cent - dissolve 25 grams of c.p. sodium peroxide (Parr) in 300-400 ml. water. Do not use any other grade. The solution is filtered through a medium grade fritted glass filtering crucible. The filtrate must be water white and is diluted to 500 ml. This solution should be kept no longer than 7 days.

Procedure:

1. From a sample solution containing hexavalent T in the form of sulfate, nitrate or fluoride, pipette an aliquot which will contain less than 100 mg. T into a 50 ml. volumetric flask.*

2. Add 15 ml. of 5 per cent sodium peroxide and dilute to the mark. Shake well.

---

* Samples which fail to react with sodium peroxide solution at this point may be treated as follows:

1. Introduce into the volumetric flask a reasonable aliquot of sample and 2-3 ml. of 30 per cent hydrogen peroxide. Warm on a hot plate until solution appears turbid.

2. Add 15 ml. of 5 per cent sodium peroxide and proceed as in steps 2, 3, and 4 above.

3. Determine the transmission against distilled water at 410 mu. with the Cenco Photelometer or other photoelectric colorimeter. (See Procedure 7.5).

4. Determine the amount of T present by means of a calibration curve similarly determined.

Calculations:

$$\frac{\text{Wt. of T in sample (mg.)}}{\text{Vol. of sample aliquot (ml.)}} = \text{mg. T/ml. of sample}$$

% TRANSMISSION

MILLIGRAMS OF "A"
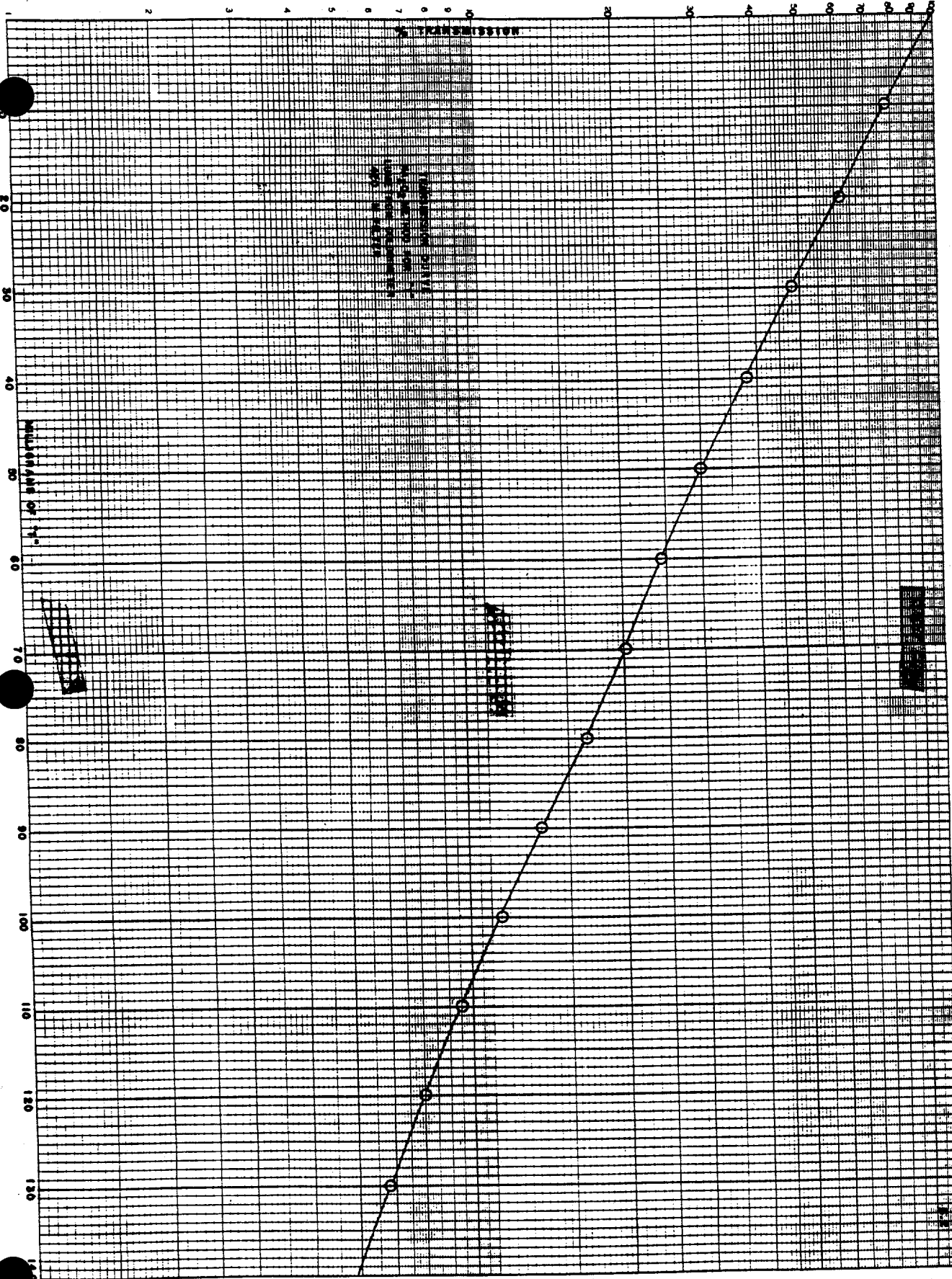
DETERMINATION OF SMALL AMOUNTS OF T IN ASH SAMPLES

(ALKALI AND ALKALINE EARTH FLUORIDES)

Method:

The T is extracted as sodium perturballate from the ash samples (high in alkali and alkaline earth fluorides) with a solution of sodium hydroxide and sodium peroxide, and measured colorimetrically with a Lumetron colorimeter, model 402 E, fitted with an M-420 blue filter.

Reagents:

1. Sodium hydroxide solution, 5 per cent

2. Sodium peroxide, c.p. (Parr)

3. Hydrogen peroxide c.p., 30 per cent

Procedure:

A. Extraction:

1. Thoroughly mix a representative sample of the ash, breaking all lumps with a stirring rod or spatula.

2. Weigh out two 1.000 $\neq$ 0.001 gram samples.

3. Place each sample in a 250 ml. beaker, and add 25 ml. of 5 per cent sodium hydroxide solution, 25 ml. of distilled water, and about 0.5 gram of sodium peroxide to each.

4. Heat to active boiling on a hot plate and maintain the boiling for two hours. The solution must not evaporate to dryness; distilled water is added from time to time to replace evaporation losses.

5. After boiling for two hours, filter the hot solution directly into a 250 ml. volumetric flask using one per cent sodium hydroxide as a wash.

6. After filtering, wash the residue from the filter paper back into the original 250 ml. beaker. This is most easily done by piercing the filter paper at the apex of the cone and washing the residue through the funnel stem with a strong stream of water from a wash bottle.

7. To the collected residue, add 25 ml. of 5 per cent sodium hydroxide and about 0.5 gram of sodium peroxide. Boil the mixture for two hours.

8. Filter this second extract into the volumetric flask containing the first extract.

9. Collect the residue as before and extract again at active boiling for four hours. Filter the third extract into a second 250 ml. volumetric flask.

B. Measurement of Transmission:

1. Dilute the two solutions to volume with distilled water add 2-3 drops of 30 per cent hydrogen peroxide and measure the transmission of each with the Lumetron Colorimeter Model 402 E. (See "Operation of the Lumetron Colorimeter, Model 402 E", Procedure 7.4).

2. Obtain the T content of the extracts from Table I which gives the per cent T corresponding to the per cent transmission in a solution volume of 250 ml. and an initial sample weight of one gram.

3. Add the amount of T in the various extracts to obtain the total T content. If the amount of T in the third extract is over 0.2 of a per cent, a fourth extraction of 4 hours may be needed. In general, ash samples of more than 3 per cent T require longer extraction.*

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* For a series of samples of the same type and approximate composition, the number of extractions may be standardized and the testing for completeness of extraction eliminated.

NOTE: If the ash samples contain considerable copper, colloidal hydrated copper hydroxide may pass through the filter paper on filtering hot. In such cases let the samples cool and stand for 1-2 hours before filtering to cause the copper hydroxide to flocculate. This method is inoperable in the presence of interfering impurities such as vanadium etc.

TABLE I

The following table gives the per cent T corresponding to the per cent transmission for a sample weight of one gram and a solution volume of 250 ml. This table is to be used in determining T by the method of extraction with sodium hydroxide and sodium peroxide.

Transmission	Per Cent T	Transmission	Per Cent T	Transmission	Per Cent T
31.2	5.00	40.5	3.80	53.2	2.60
31.6	4.95	41.0	3.75	53.9	2.55
32.0	4.90	41.4	3.70	54.6	2.50
32.4	4.85	41.8	3.65	54.9	2.48
32.7	4.80	42.2	3.60	55.2	2.45
33.0	4.75	42.7	3.55	55.5	2.43
33.3	4.70	43.2	3.50	55.8	2.40
33.7	4.65	43.8	3.45	56.1	2.38
34.1	4.60	44.3	3.40	56.4	2.35
34.5	4.55	44.8	3.35	56.7	2.33
34.9	4.50	45.3	3.30	57.2	2.30
35.3	4.45	45.8	3.25	57.5	2.28
35.7	4.40	46.3	3.20	57.9	2.25
36.1	4.35	46.9	3.15	58.2	2.23
36.5	4.30	47.6	3.10	58.6	2.20
36.9	4.25	48.2	3.05	58.9	2.18
37.3	4.20	48.9	3.00	59.3	2.15
37.7	4.15	49.4	2.95	59.7	2.13
38.1	4.10	50.0	2.90	60.0	2.10
38.5	4.05	50.6	2.85	60.4	2.08
38.9	4.00	51.1	2.80	60.8	2.05
39.3	3.95	51.6	2.75	61.2	2.03
39.7	3.90	52.1	2.70	61.5	2.00
40.1	3.85	52.6	2.65	61.9	1.98

TABLE I (cont'd.)

Transmission	Per Cent T	Transmission	Per Cent T	Transmission	Per Cent T
62.3	1.95	73.1	1.28	85.5	0.63
62.6	1.93	73.6	1.25	86.0	0.60
63.0	1.90	74.0	1.23	86.5	0.58
63.4	1.88	74.5	1.20	87.0	0.55
63.8	1.85	74.9	1.18	87.5	0.53
64.2	1.83	75.4	1.15	88.0	0.50
64.6	1.80	75.8	1.13	88.5	0.48
65.0	1.78	76.3	1.10	89.1	0.45
65.4	1.75	76.7	1.08	89.6	0.43
65.7	1.73	77.1	1.05	90.2	0.40
66.1	1.70	77.5	1.03	90.7	0.38
66.4	1.68	78.0	1.00	91.3	0.35
66.8	1.65	78.5	0.98	91.8	0.33
67.2	1.63	79.0	0.95	92.4	0.30
67.6	1.60	79.5	0.93	93.0	0.28
68.0	1.58	80.0	0.90	93.6	0.25
68.4	1.55	80.5	0.88	94.2	0.23
68.8	1.53	81.0	0.85	94.8	0.20
69.2	1.50	81.5	0.83	95.7	0.18
69.6	1.48	82.0	0.80	96.1	0.15
70.0	1.45	82.5	0.78	96.7	0.13
70.4	1.43	83.0	0.75	97.4	0.10
70.9	1.40	83.5	0.73	98.0	0.08
71.3	1.38	84.0	0.70	98.7	0.05
71.8	1.35	84.5	0.68	99.3	0.03
72.2	1.33	85.0	0.65	100.0	0.00
72.7	1.30				

DETERMINATION OF T IN SPENT CARBON AND THE PREPARATION

OF T_3O_8 FOR QUALITY (ISOTOPIC) ASSAY

Method:

The carbon is separated from the alumina (corundum) and then fused with sodium nitrate in order to destroy the carbon and any organic material which may be present. The fused mass is dissolved in 50 per cent nitric acid and boiled to insure complete oxidation of the T to the hexavalent state. Any iron or aluminum in solution is precipitated with ammonium carbonate and filtered while the T remains in solution as a soluble carbonate complex. The T is determined by the sodium peroxide colorimetric method using the Cenco Photelometer or other colorimeter. The oxide is prepared by precipitating the T with ammonium hydroxide, filtering, and igniting in a platinum crucible over a blast burner.

Reagents and Apparatus:

1. Triethanolamine and ethanol mixture, 1:1

2. Sodium nitrate

3. Nitric acid 50 per cent

4. Ammonium hydroxide, concentrated

5. Ammonium carbonate

6. Sulfuric acid 10 per cent

7. Sodium peroxide solution 5 per cent - Dissolve 25 grams of c.p. sodium peroxide (Parr) in 300-400 ml. of distilled water. Filter through a glass frit and dilute to 500 ml. Do not keep for more than 7 days.

Procedure:

A. Separation of Carbon from Alumina: - The sample may consist of a mixture of carbon and alumina particles, in which case the carbon must be separated.

1. Weigh the entire sample of mixture as received (50 grams or more). A platform balance may be used for this weighing.

2. Assemble a nest of standard sleeves (Nos. 4, 8 and 16) with a pan at the bottom. Pour the sample weighed above into the topmost sieve and shake the nest until all of the material has been separated on the sieves according to particle size.

3. The material caught in each segment of the nest is then separated manually as follows. Pour one fraction into a pan. Hold the pan in a slightly inclined position and sweep the mixture with a brush. Brushing will cause the cylindrical carbon pellets to roll to the bottom and away from the irregular shaped alumina particles which remain in their original position. The carbon is then collected from all fractions and weighed.

4. Calculate the percentage composition of the original mixture from its initial weight and the weight of the separated carbon. NOTE: The alumina, except in the case of activated alumina, is usually discarded inasmuch as it has been found to absorb very little T and makes no substantial contribution to the T content within the limits of accuracy usually required in this determination. If activated alumina or ordinary alumina known to contain large amounts of T is present, the alumina must also be analyzed for T by a different procedure.

B. Preparation of the Sample:

1. Weigh a ten gram sample of carbon into a platinum dish of suitable
   size.

2. Cover the sample in the dish with a 1:1 mixture of triethanolamine
   and ethanol.

3. Ignite the mixture carefully over a burner.

4. After the solvent has burned off, add sodium nitrate in small
   portions to the residue in the dish and fuse the mixture until all
   of the organic matter has been destroyed.

5. Dissolve the fused mixture in the smallest possible quantity of 50
   per cent nitric acid (approximately 100-150 ml. in a 1 liter beaker).

6. Boil the solution for ten minutes to insure oxidation of any lower
   valence states of T to the hexavalent state.

7. Filter off any insoluble material in the solution through a No. 42
   Whatman filter paper.

8. Neutralize the nitric acid solution with ammonium hydroxide to a pH
   of 6. Add solid ammonium carbonate until the pH of the solution
   is 8-9.

9. Boil for two minutes. If the ammonium carbonate has been destroyed
   by thermal decomposition, add additional solid salt since an excess
   of carbonate must be present in order not to lose any of the T by
   precipitation.

10. The ferric hydroxide or aluminum hydroxide which precipitates at
    this point if any iron or aluminum is present in the sample is removed
    by filtration using a No. 42 Whatman filter paper. The filtrate
    contains the T which is present as the soluble carbonate complex.

11. Wash the carbonate precipitate with saturated ammonium carbonate solution until a potassium ferrocyanide spot test shows that the washings no longer contain any T. The test is carried out as described in (1) below. The filtrate and washings are also tested for iron using the thiocyanate test as outlined below in (2) in order to insure that the carbonate separation has been effective.

(1) The solution to be tested should have a pH of 5-6. Add a small quantity of 3 per cent potassium ferrocyanide solution to the solution to be tested. A brown color indicates the presence of T. Copper gives a red color and iron a blue or green color. It is, therefore, necessary that these interfering elements be removed before testing.

(2) The solution to be tested should be slightly acid (pH 5). Add a few drops of 1 N potassium thiocyanate solution to the slightly acid solution to be tested. A red color indicates the presence of iron.

C. Determination of T in the Sample:

1. Transfer the filtrate and washings, obtained in 10 and 11 of Part B above, quantitatively to a 500 ml. volumetric flask and make the solution up to volume with distilled water.

2. A suitable aliquot of this solution is then analyzed for T by the Sodium Peroxide Colorimetric Method using the Cenco Photelometer or other photoelectric colorimeter (See Procedure 6.2).

3. From the quantity of T found in the aliquot, calculate the percentage of T present in the original sample.

Calculations:

$$\frac{\text{Mg. T in aliquot} \times \dfrac{\text{Total volume of sample solution}}{\text{Volume of aliquot}}}{\text{Sample weight (mg.)}} \times 100 = \text{\% T in sample}$$

D. The Preparation of T_3O_8 for Quality (Isotopic) Assay:

NOTE: A sample of not less than 150 milligrams is required for the quality assay. Prepare a 1 gram sample if possible.

1. Take an appropriate volume of the solution obtained in 1 Part C to insure an adequate sample. Acidify the solution with 50 per cent nitric acid and boil to insure complete removal of carbon dioxide.

2. To the warm, acid, carbon dioxide-free solution add ammonium hydroxide in slight excess to precipitate the T.

3. Filter the precipitate on a No. 42 Whatman filter paper. For convenience in handling the large precipitate use a Buchner funnel.

4. After the precipitate has been washed, dissolve it off the paper with approximately 20 ml. of 10 per cent sulfuric acid.

5. Wash the paper with three 10 ml. portions of water.

6. Heat the combined solution and washings on the hot plate until copious fumes of SO_3 are evolved.

7. Allow to cool and dilute the residue with 20 ml. of distilled water.

8. Filter to remove any insoluble matter. If soluble silica was present it will be removed in this step.

9. Add ammonium hydroxide to the filtrate until all of the T has been precipitated.

10. Filter the precipitate on a No. 42 Whatman filter paper and wash.

11. Remove the filter paper and precipitate from the funnel and transfer to a platinum crucible or dish.

12. Ash the filter paper. Heat the crucible and contents over a Meker burner or compressed air burner until the T has been converted to T_3O_8. This oxide is dark green to black in color. (Orange or other colors indicate extensive impurities present in the preparation).

13. Dissolve a small quantity of the oxide in 50 per cent nitric acid. If there is any evidence of acid-insoluble material in the sample, the entire sample of oxide must be redissolved in nitric acid, filtered, reprecipitated, and ignited as described in Steps 7 to 12 above.

14. If the sample passes this solubility test, it is weighed and transferred to a clean, dry bottle for shipment to the quality assay laboratory.

DETERMINATION OF T IN MFL AND 2144

Method:

The contaminated lubricant (high molecular weight fluorocarbons) is ignited and fused with sodium nitrate in order to decompose any organic material which may be present. The fused mass is dissolved in 50% nitric acid and boiled to insure complete oxidation of the T to the hexavalent state. Any iron or aluminum in solution is precipitated with ammonium carbonate and filtered off while the T remains in solution as a soluble carbonate complex. The T is determined by the sodium peroxide colorimetric method using the Cenco Photolometer or other photoelectric colorimeter.

Reagents:

1. Triethanolamine and ethanol mixture - 1:1

2. Sodium nitrate

3. Nitric acid, 50%

4. Ammonium hydroxide, concentrated

5. Ammonium carbonate, c.p.

6. Sodium peroxide solution - 5% - Dissolve 25 grams of c.p. sodium peroxide (Parr) in 300-400 ml. of distilled water. Filter through a glass frit and dilute to 500 ml. Do not keep for more than 7 days.

Procedure:

A. Preparation of the Sample:

1. Weigh a twenty-five gram sample of the contaminated lubricant into a platinum dish of suitable size.

2. Cover the sample in the dish with 1:1 mixture of triethanolamine and ethanol.

3. Ignite the mixture in the dish carefully over a burner.

4. After the solvent has burned off, add sodium nitrate in small portions to the residue in the dish and fuse the mixture until all of the organic matter has been destroyed.

5. Dissolve the fused mixture in the smallest possible amount of 50% nitric acid (approximately 100-150 ml. in a 1 liter beaker).

6. Boil the solution for ten minutes to insure complete oxidation of any lower valence states of T to the hexavalent state.

7. Filter off any insoluble material in the solution through a No. 42 Whatman filter paper.

8. Neutralize the nitric acid solution with ammonium hydroxide to a pH of 6. Add solid ammonium carbonate until the pH of the solution is 8-9.

9. Boil for two minutes. If the ammonium carbonate has been destroyed by thermal decomposition, add additional solid salt since an excess of carbonate must be present in order not to lose any of the T by precipitation.

10. The ferric hydroxide or aluminum hydroxide which precipitates at this point if any iron or aluminum was present in the sample is removed by filtration using a No. 42 Whatman filter paper. The filtrate contains the T which is present as a soluble carbonate complex.

11. Wash the carbonate precipitate with saturated ammonium carbonate solution until a potassium ferrocyanide spot test shows that the washings no longer contain any T. The test is carried out as described in (1) below. The filtrate and washings are also tested for

-3-

iron using the thiocyanate test as outlined below in (2) in order to insure that the carbonate separation has been effective.

(1) The solution to be tested should have a pH of 5-6. Add a small quantity of 3% potassium ferrocyanide solution to the solution to be tested. A brown color indicates the presence of T. Copper gives a red color and iron a blue or green color. It is therefore necessary that these interfering elements be removed before testing.

(2) The solution to be tested should be slightly acid (pH5.) Add a few drops 1 N. potassium thiocyanate solution to the slightly acid solution to be tested. A red color indicates the presence of iron.

B. Determination of T in the Sample:

1. Transfer the filtrate and washings obtained in 10 and 11 of Part A above quantitatively to a 500 ml. volumetric flask and make the solution up to volume with distilled water.

2. A suitable aliquot of this solution is then analyzed for T by the sodium peroxide Colorimetric method using the Cenco Photelometer. (A description of this method is given in Procedure 6.2).

3. From the quantity of T found in the aliquot, the percentage of T present in the original sample is calculated.

Calculations:

$$\frac{\dfrac{mg. T\ in\ aliquot}{aliquot\ volume\ (ml.)} \times 500*}{sample\ wt.\ (mg.)} \times 100 = percent\ T\ in\ sample$$

* Volume of filtrate

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VOLUMETRIC METHOD FOR THE QUANTITATIVE ANALYSIS OF "T"

Method 5A (Revised)

Apparatus

Pipets, balance, beakers, filter funnels, filter paper, watch glasses, 500 ml. Erlenmeyer flask, wash bottles, Jones reductor.

Reagents and Solutions:

Concentrated sulfuric acid, concentrated nitric acid, anhydrous sodium carbonate, 2% sodium carbonate solution, concentrated ammonium hydroxide, a dilute carbonate-free ammonia solution, 0.1 N potassium permanganate solution diphenylamine sulfonic acid indicator solution, a solution which contains 1.6% ferric chloride and 30% syrupy phosphoric acid, a standard 0.02 N potassium dichromate solution.

Preparation of Sample:

Before sampling, be sure that the sample is as homogeneous as possible. In case of a solid, it may be necessary to pulverize the sample in a mortar. If a liquid is to be analyzed, simply shake the sample bottle and use a pipet to remove a suitable aliquot.

Some liquid samples contain much insoluble matter or immiscible liquids. If homogeneity can be obtained by shaking the sample into a uniform emulsion or suspension the sample may be removed with a pipet. However, if the two phases separate too rapidly or if the solid matter contains too many large particles weigh out the entire contents of the sample bottle and take it through the procedure until a point is reached where the sample is totally in solution. Then transfer it to a volumetric flask, dilute to the mark, and remove a suitable aliquot with a pipet. Continue the procedure on this aliquot.

Use, as a rule, a sample weight or volume which contains between 0.02 and 0.1 g. of T. However, there are other factors governing sample size. Any aliquot of a clear solution up to 200 ml. can be analyzed but no smaller aliquot than 50 ml. should ever be taken from even the most homogeneous suspension, or emulsion. As for uniform solids, any convenient weight between 0.25 and 10 g. may be used. If there is some doubt as to the uniformity of the sample, use a minimum of 1 g.

Procedure:

A-Liquids:

Transfer an aliquot of the liquid by pipet to a 250 ml. beaker. If the solution is alkaline, neutralize with concentrated sulfuric acid. Then add 10 ml. of concentrated sulfuric acid, 5 ml. of concentrated nitric acid, and 5 ml. of concentrated hydrochloric acid, cover the beaker with a watch glass and boil this solution down to white SO_3 fumes on the hot plate.

B-Solids:

Weigh out the sample in a 250 ml. beaker to 4 significant figures. Add dilute sulfuric acid to dissolve all the readily soluble material and and then add 10 ml. of concentrated nitric acid, and 5 ml. of concentrated hydrochloric acid. Cover the beaker with a watch glass and boil the sample down to SO_3 fumes on the hot plate.

From this point, the procedure is the same for either the solid or liquid samples. Cool the sample and dilute slowly with distilled water, stirring to minimize splattering and to effect solution of the salts which tend to crystallize out. Add small portions of anhydrous sodium carbonate to the point where addition of a few crystals ceases to cause

effervescence and then add about 1 g. in excess. Add macerated filter paper to the beaker and boil the suspension for about 1 minute. Filter the hot suspension through #42 Whatman filter paper or its equivalent and wash the residue beaker and watch glass at least three times with hot 2% sodium carbonate solution. Collect the filtrate and washings in a 400 ml. beaker and discard the residue.

To the filtrate add 5 ml. of concentrated sulfuric acid. At this point the solution should be acid. Check this with indicator paper. If the solution is still alkaline add more acid; then, if necessary, bring solution up to 200 ml. with distilled water. Cover beaker with a watch glass, boil the solution for 15 minutes, remove from the hot plate and add concentrated ammonium hydroxide slowly and with stirring until the yellow gelatinous precipitate $NH_4T_2O_7$ appears. Add macerated filter paper plus a 5 ml. excess of concentrated ammonia. Boil for 1 minute and filter the hot suspension through #42 Watman filter paper or its equivalent catching filtrate in a 400 ml. beaker. Wash the watch glass, beaker, and precipitate at least 3 times with a carbonate-free 2% ammonia solution. This solution is prepared by adding concentrated ammonia to freshly boiled distilled water. Discard filtrate and washings. Pour 100 ml. of 1:9 sulfuric acid into the beaker in which the precipitation occurred, heat to about 60°C and pour the acid through the filter, catching the dissolved T in a 250 ml. beaker. If necessary, wash with more warm 1:9 sulfuric acid. After this filtrate has been cooled to room temperature, add 0.1 N potassium permanganate solution dropwise until the first faint permanent pink coloration appears.

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At this point run a blank on the Jones reductor. Add 0.1 N potassium permanganate dropwise to 100 ml. of 1:9 sulfuric acid and run the solution through the reductor under slight vacuum into a 500 ml. Erlenmeyer flask. Wash the Jones reductor with about 250 ml. of 1:9 sulfuric acid and collect these washings in the same flask. Add 50 ml. of the ferric chloride - phosphoric acid solution, 8 drops of diphenylamine sulfonic acid indicator, and titrate with standard potassium dichromate solution to the appearance of a faint violet color. This blank should run no higher than two drops. If the blank is too high wash the reductor once again with dilute sulfuric acid. If the blank is still too high, re-charge the reductor tube. If the blank is satisfactory, pass the sample through it and wash the reductor with 250 ml. of 1:9 sulfuric acid. Collect the reduced sample and washings in a 500 ml. Erlenmeyer flask and bubble air through it for at least 5 minutes to bring all the T up to the tetravalent state. Then add 50 ml. of the ferric chloride - phosphoric acid solution and 8 drops of the diphenylamine sulfonic acid indicator. Titrate with the standard potassium dichromate solution to the point where the color changes from pale green to the first faint per-manent violet.

Calculations:

a) Liquids:

$$\frac{(ml. \text{ of } K_2Cr_2O_7 - ml. \text{ blank})(Normality \text{ of } K_2Cr_2O_7)(119)}{ml. \text{ of sample}} = g. \text{ of T per liter}$$

b) Solids:

$$\frac{(ml. \text{ of } K_2Cr_2O_7 - ml. \text{ blank})(Normality \text{ of } K_2Cr_2O_7)(0.119)(100)}{\text{Weight of Sample}} = \% \text{ T}$$

Notes:

a) Do not allow the Jones reductor to run dry before, during, or after use.

b) One liter of the ferric chloride - phosphoric acid solution contains 26.6 g. of $FeCl_3$ 6 H_2O and 300 ml. of 85% $H_3 PO_4$.

DETERMINATION OF "T" IN CAUSTIC SCRUBBER

Method 5 ASC

Sample Size and Preparations

Pipet 100 ml. of the well-mixed sample into a 600 ml. beaker and dilute to 250-300 ml. with distilled water; add HCl until acid to litmus paper. Then add 2-3 g. of Na_2CO_3. After the Na_2CO_3 has dissolved add a strong solution of $CaCl_2$ to complete precipitation of all fluorides as CaF_2, plus a few ml. in excess. Then neutralize with HCl and add 2-3 ml. in excess, place on a hot plate and digest at a low heat with frequent stirring for a couple of hours or allow the samples to digest overnight.

If allowed to stand overnight, heat to almost boiling and while hot slowly add concentrated H_2SO_4 to complete precipitation of all excess calcium. Usually 25 ml. of the H_2SO_4 is sufficient to cause complete precipitation.

The samples are next cooled in a cold water bath to crystallize all salts and to lower solubility of CaF_2. Filter through #42 filter paper. Wash precipitate five or six times with 5% H_2SO_4 solution.

Boil down the clear filtrate to a volume where the salts begin to drop out of solution, cool again in a cold water bath and filter off precipitated salts using a #1 filter paper; wash precipitate with 5% H_2SO_4 solution. Precipitate the iron as in Method 5A. After boiling cool as above and filter as regular iron precipitate. Then follow Method 5A for remainder of determination.

DETERMINATION OF "T" IN OIL SAMPLES

Method 5 AOL

Application of Method

This procedure is now used for all oil samples.

Preparation of Sample

The sample is stirred vigorously to obtain a uniform sample. When large particles are evident in the sample they are broken up as thoroughly as possible by the aid of a stirring rod.

The sample is then weighed into a porcelain crucible using from 5-25 grams depending on its apparent "T" content.

The crucibles are placed on a wire gauze over a hot plate, and should be watched carefully at the beginning to avoid possible foaming or frothing which might cause them to spill over.

Heat until all fuming has stopped and only heavy charred oil or carbon residue remains. Remove from hot plate and burn off any carbon or oil present over the flame of a Bunsen or Meker burner.

The residue in the crucible is now transferred by using concentrated H_2SO_4 to a 250 ml. beaker. Approximately 5 ml. HNO_3 is added and the solution heated to evolution of SO_3 fumes.

If necessary additional HNO_3 may be added in order to remove the last remaining carbon.

After cooling, the watch glass and sides of beaker are washed with distilled water and the solution is diluted to approximately 125 ml.

From here on continue with Method 5A as the iron precipitation.

DETERMINATION OF T IN CONVERTER SAMPLES

Sample Size:

The process gas is sampled and dissolved as described in the procedure for taking Converter Samples and is received in the laboratory as a dilute sulfuric acid solution of T. Dilute the sample to 250 ml. in a volumetric flask with distilled water and choose an aliquot containing between 0.02 and 0.1 g. of T. If the sample is dilute with respect to T, it may be necessary to evaporate the sample down to 90 ml.

Take the aliquot or evaporated sample and convert it to a 100 ml. solution which contains 10% sulfuric acid by volume.

Procedure:

Reduce, aerate and titrate as in Procedure 5A.

Calculations:

1. $mg. T = (ml. of K_2Cr_2O_7 - reductor blank)(K_2Cr_2O_7 normality)(119)$

2. $Mole \% T = \dfrac{(mg. T in aliquot)(273 + t^oC.)(6550)}{(vol. of bulb in ml.)(press. in mm.)(ml. of aliquot)}$

PREPARATION AND USE OF THE JONES REDUCTOR

Reagents and Apparatus:

1. Jones reductor column (See Figure 1)

2. Zinc, 20-30 mesh, c.p.

3. Dilute hydrochloric acid (3 N)

4. Mercuric chloride solution (25 grams per liter)

5. Aspirator

6. Filtering flasks, pyrex 500 ml.

Procedure:

A. Preparation of the Reductor:

1. Cover 800 grams of 20 to 30 mesh zinc with 3 N hydrochloric acid, and add 400 ml. of mercuric chloride (25 grams/liter) solution while stirring the zinc, until the evolution of hydrogen ceases.

2. In the bottom of the reductor tube, place a perforated disk or some pieces of glass. On this place a wad of glass wool, and then a little asbestos suspension. If the asbestos layer is too thick, the reductor is likely to become clogged and if it is too thin, some zinc powder may run through and interfere with the analysis.

3. Fill the remainder of the reductor tube with well washed, amalgamated zinc.

B. Use of the Reductor:

1. Add 100 ml. of 1 N sulfuric acid through the funnel (B) with the stopcock (C) open. Use a slight suction.

2. When most of the acid has drained through (do not let the level of the acid solution fall below the top of the zinc column), add the solution to be reduced.

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3. When the level of the solution falls to within a few cm. of the top of the zinc column add 250 ml. of 1 N sulfuric acid. Wash the sample beaker with this acid. Add it to the reductor in small portions.

4. Pass 100 ml. of distilled water through the reductor. At no time should air be allowed to enter the filled portion of the reductor tube.

5. Keep the reductor tube filled with water and covered when not in use.

FIGURE 1

JONES REDUCTOR COLUMN
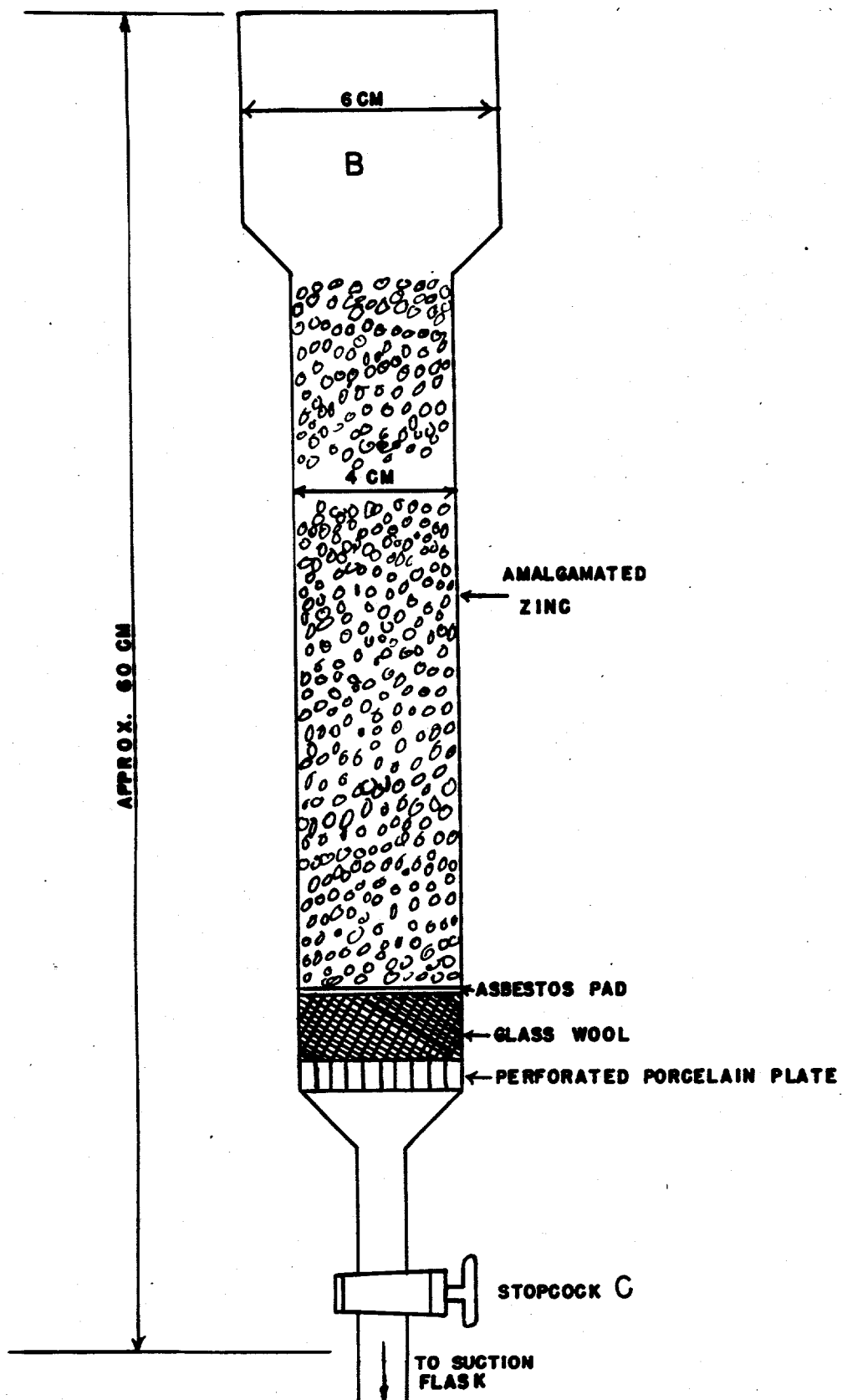
STANDARDIZATION OF CERIC AMMONIUM SULFATE AGAINST
SODIUM OXALATE

Method:

Carefully weighed sodium oxalate samples are dissolved in dilute sulfuric acid and titrated with ceric sulfate solution using ortho phenanthroline-ferrous complex as indicator. The titration is carried out by adding an excess of ceric sulfate and back-titrating the excess with ferrous ammonium sulfate to a pink end-point.

Reagents and Apparatus:

1. Sodium oxalate (U.S. Bureau of Standard Grade) Dry the salt at 105°C for 2-3 hours before use.

2. Dilute sulfuric acid (2N).

3. Ortho phenanthroline indicator - dissolve sufficient ortho phenanthroline in 0.025M ferrous sulfate to make the solution 0.075 M with respect to the indicator. Warm to dissolve.

4. Ceric ammonium sulfate solution - dissolve sufficient ceric ammonium sulfate in 1 M sulfuric acid to make a 0.05 N ceric solution. The solution should stand at least two weeks before standardizing and should be filtered before using.

5. Ferrous ammonium sulfate solution - dissolve sufficient ferrous ammonium sulfate in 1 M sulfuric acid to make a 0.05 N solution.

Procedure:

1. Weigh 0.1300 - 0.1400 gram portions of sodium oxalate into each of three 600 ml. beakers.

2. To each beaker add 200 ml. of 2 N sulfuric acid and 150 ml. of distilled water.

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3. Dissolve the sodium oxalate. Add 45-50 ml. of the ceric ammonium sulfate to be standardized to each of the beakers.

4. Heat to 60°C. on a hot plate and then cool to room temperature. (Do not titrate the solutions while warm, since the end-point given by the ortho phenanthroline complex will be erratic.)

5. Add 2 drops of othro-phenanthroline complex indicator and titrate to a salmon pink end-point with the ferrous ammonium sulfate solution.

6. Carry out a cross titration as follows:

    Acidify 20-25 ml. of the ceric ammonium sulfate wolution with 200 ml. of 2 N sulfuric acid and dilute with 100 ml. of water.

7. Add 2 drops of othro-phenanthroline complex indicator and titrate with ferrous ammonium sulfate to a salmon pink end-point as before.

8. Calculate the cross titer: Divid the volume of ceric ammonium sulfate used by the volume of ferrous ammonium sulfate used.

9. Using the cross titer value, calculate the normality of the ceric ammonium sulfate.

Calculations:

$$\text{Normality of ceric sulfate} = \frac{\text{Weight of sodium oxalate}}{(A - B \text{ cross titer}) \times \text{Me.}}$$

A = ml. of ceric ammonium sulfate used.

B = ml. of ferrous ammonium sulfate used in back titrating the excess ceric ammonium sulfate.

Me. = millequivalent weight of sodium oxalate (0.0670).

OPERATION OF THE MERCURY CATHODE CELL

Method:

A sulfuric acid solution of T-sulfate, containing metal impurities such as iron, copper, nickel and other cations which are deposited quantitatively in a mercury cathode, is electrolyzed in a water-cooled cell using a platinum anode. After a spot test shows that the undesired metal has been removed from solution, the mercury amalgam and pure reduced T solution are drained from the cell and separated simultaneously.

Reagents and Apparatus:

1. Mercury cathode cell, water jacketed. (See figure 1).

2. Platinum anodes - platinum gauze about 4" x 5", curved to fit within the cathode cell.

3. Distilled mercury.

Procedure:

1. Fill the cell with sufficient distilled mercury to bring its surface to within one centimeter of the platinum gauze anode. About 2 to 2.5 Kg. of mercury will usually suffice.

2. Transfer the sample (dissolved in 10 per cent sulfuric acid and free from nitrates) carefully to the cell. Start cooling water through the jacket.

3. With the sample in the apparatus, the stirrer is lowered below the mercury surface to give a smoothly rotating cathode. "Swirling" of the mercury surface should be avoided because some solution may be trapped below the mercury surface.

4. Electrolyze the sample at 3 to 3.5 amperes for one hour. (Note: Be sure the two way stopcock is turned so that the electrical circuit is complete. This is ample time for removal of amounts of

impurities to the extent of 5 per cent in the original sample. If the amounts of impurity are excessive a longer period is required.

5. After one hour, stop the agitator and _immediately_ (with the current still _on_) open the _bottom_ stopcock. Drain the mercury from the cell slowly to prevent the solution from being sucked out with the mercury.

6. When the ammeter reads zero, the solution is no longer touching the anode.

7. Drain the rest of the mercury by means of the two-way stopcock leaving a drop or two in the capillary of the stopcock. Do not allow any solution to come out with the mercury.

8. When the mercury has been removed, drain the sample into a separate beaker and wash the cell with water, collecting the washings with the sample. Filter the sample immediately to remove the drop of mercury and other foreign matter.

FIGURE I
MERCURY CATHODE

ANODE HANGS HERE

WIRE TO CATHODE

COLD WATER OUTLET

COLD WATER INLET

MERCURY

TWO WAY STOPCOCK IN THIS POSITION FOR OPERATION

ONE WAY STOPCOCK CLOSED DURING ELECTROLYSIS
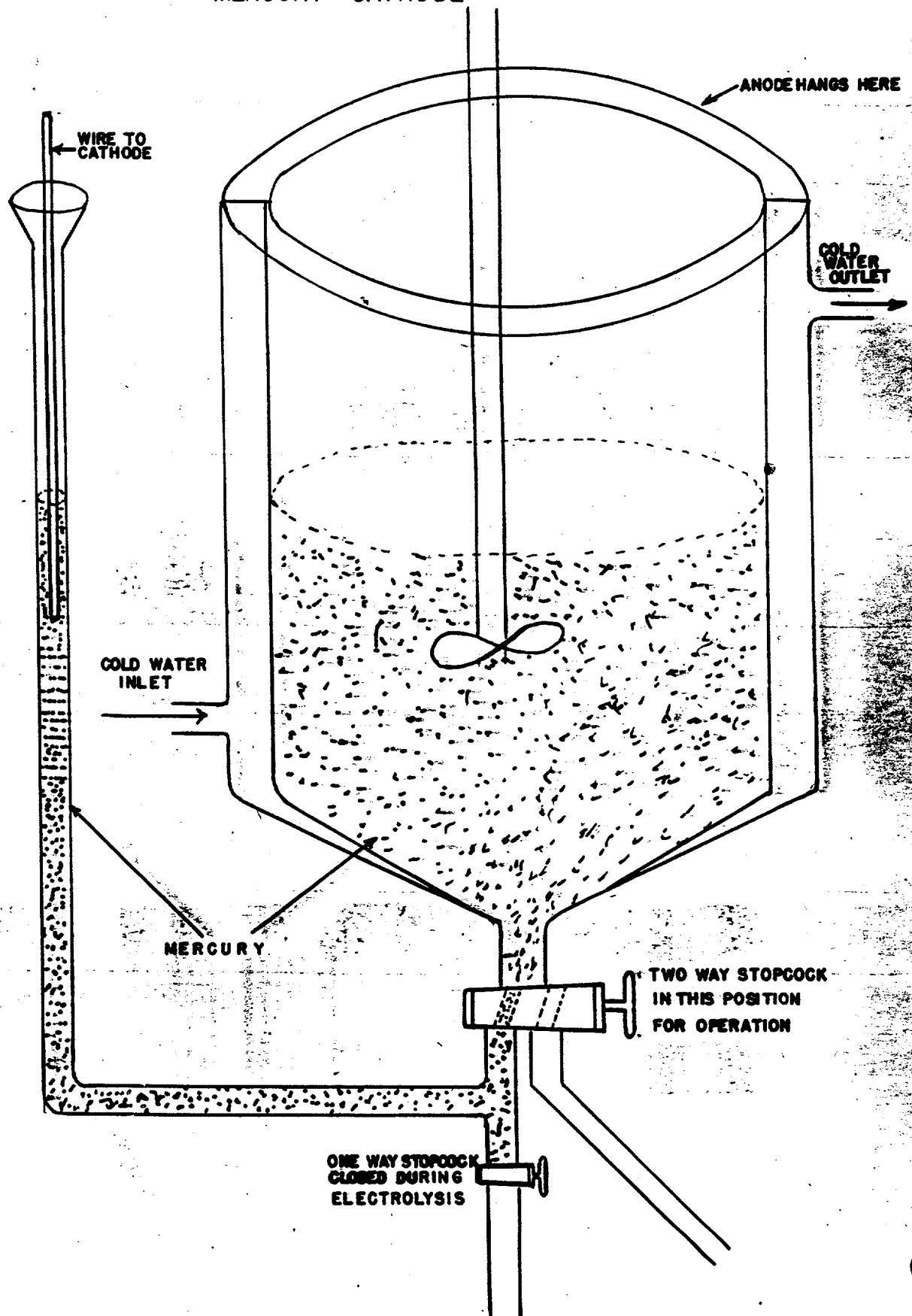
PROCEDURE FOR OPERATION OF THE LUMETRON COLORIMETER

MODEL 402 E

The following procedure describes the operation of the Lumetron Color-imeter, Model 402 E, as applied to the determination of small amounts of T by the sodium peroxide method.

Apparatus:

1. Lumetron Colorimeter, Model 402 E.

2. L-420 blue filter for above.

3. Rectangular cell with a light path of 1.0 cm. and a volume of 15 ml.

Procedure:

A. Adjustment of the Galvanometer:

1. The hair line of the galvanometer beam is set to coincide with the zero point on the scale by means of the galvanometer adjusting knob.

B. Adjustment of Lamp Intensity:

1. Turn on the colorimeter lamp and allow the lamp filament to heat for five minutes.

2. Hold the potentiometer switch in the forward position (away from the operator) and observe the deflection of the galvanometer beam. The amount of deflection observed depends upon the lamp intensity.

3. Adjust the lamp intensity by means of the lamp rheostat to give a deflection 10 units left of the galvanometer zero point.

C. Adjusting the Zero Point:

1. Fill the cell with distilled water for use as a blank; wipe the glass faces carefully with Kleenex to remove adherent moisture.

2. Place the cell in the colorimeter on the right side of the cell com-partment (near the photoelectric cell).

3. Set the calibrated dial to read 100; hold the potentiometer switch back (toward the operator); and note the deflection of the galvanometer. If the colorimeter is properly adjusted the galvanometer beam will not deflect from the zero position. If, however, the galvanometer beam does not remain at zero, slowly bring the beam to zero position by turning the balance cell dial. The colorimeter is then adjusted for measuring light transmission to the T solutions.

D. Measuring the Transmission of T Solutions:

1. Rinse the cell three times with the solution to be tested.

2. Fill the cell to about 0.5 cm. from the top; wipe carefully with (Kleenex) and place it in the colorimeter. Hold the potentiometer switch back (toward the operator), and observe the galvanometer deflection.

3. Turn the calibrated dial until the galvanometer index returns to the "zero position". In this position the colorimeter is in balance.

4. Read the percent transmission directly from the calibrated dial.

PROCEDURE FOR OPERATION OF CENCO PHOTELOMETER

Apparatus:

1. Cenco-Sheard-Sanford Photelometer, with transformer for 110 V. AC.

2. Complete set of filters (see below).

3. 1 cm. cells for above.

Procedure:

1. Place the proper filter in position in the instrument.

   Filters available:

Filter No.	Maximum Transmission in Millimicrons
A	410
B	525
C	610
D	645

2. Place the cell containing distilled water or other blank in the central compartment of the cell holder and place it in the light path.

3. With the "lights" switch "off", check the zero reading of the instrument. If the reading is not zero, adjust it as follows:

   With a piece of opaque cardboard in front of the filter, the galvanometer pointer should be at zero. If not, turn the "adjust for zero" screw located on the nameplate of the galvanometer until the undeflected reading is zero.

4. Turn the "lights" switch to the "on" position, and turn the "meter" switch to the "on" position.

5. Set the fine adjustment knob so that the point is upward. Open the iris diaphram until the meter deflects approximately full scale.

Now use the fine adjustment control to obtain a reading of exactly
100. (This reading corresponds to exactly 100 per cent transmission).
Due to fatigue of the photocell, adjustment of the reading to 100
may be necessary from time to time.

6. Slide the cell containing the solution to be measured into the
light path.

7. Read the position of the pointer on the scale. This value should
be less than 100 and represents the light transmission for the
solution being measured.

PROCEDURE FOR OPERATION OF BECKMAN QUARTZ SPECTROPHOTOMETER

Apparatus:

1. Beckman Quartz Spectrophotometer

2. Corex cells, 1 cm. square, approximately 10 ml. capacity for above.

Procedure:

1. Turn the lamp switch to "On" position. Allow the instrument to warm up for several minutes.

2. Set the selector switch to "Check".

3. Rotate the wave length knob until the desired scale value is shown under the hairline.

4. Select the proper phototube. (The proper phototube to use is determined by the spectral range to be investigated. The red-sensitive phototube for use above 625 millimicrons is in position when the knob on the photo-tube housing is pushed "In". The blue sensitive, or ultraviolet-sensitive, phototube for use below 625 millimicrons is in position when the knob is pulled "out" as far as possible.

5. Select the proper filter. (The filter slide is located between the exit slit and the cell compartment and is operated by means of the knob on the front end. The front position, knob pushed "in", is blank and is used for measurements in the range 400 to 1000 millimicrons, (also with hydrogen tube.) The second position contains a red-purple filter and is used in the range 400 to 320 millimicrons, with the tungsten lamp. The third position is blank and fitted with a special filter for unusual applications.)

6. Turn the shutter switch to "Off" position.

7. Rotate the dark-current knob to zero the meter needle. Repeat occasionally.

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8. Make sure that the cells, previously cleaned and checked, and the holder are seated properly; then replace the compartment cover and place the sample solvent or "blank" in the light path.

9. Turn the shutter switch to the "On" position.

10. Rotate the slit knob to approximately zero the needle.

11. Rotate the sensitivity knob to accurately zero the needle. (For best performance it is suggested that the sensitivity knob to be used 1 to 3 turns from its clockwise limit. If it is desired to employ the narrow slit openings, the sensitivity knob may be used near its counter-clock limit. At this position the accuracy to which the percent transmission slide wire can be set is only 10% as compared with the higher sensitivity obtained with the knob at the clockwise limit.)

12. By means of the slider knob position the unknown sample in the light beam.

13. Set the selector switch to 1.0

14. Rotate the transmission knob to "zero" the needle.

15. Record the transmission or density reading. (Set the selector switch to 0.1 if the transmission is less than 10%. The values obtained with this setting are 1/10 those obtained with the switch at 1.0 as in (13).)

16. Place the next unknown sample in the light path and "zero" the needle by rotating the transmission knob.

OPERATION OF INFRA-RED SPECTROMETER

I. Spectrometer Unit

An electrically heated Globar (silicon carbide rod) is the source of infra-red radiation. The radiation is focussed by mirrors in the left-hand chamber onto a slit at the entrance to the right hand chamber. Absorption cells, in proper holders, are held by a slot in front of this slit. The radiation then is passed through a prism, and the desired wavelength isolated and focussed on a thermocouple.

The current from the thermocouple is in proportion to the energy of the incident radiation of the wavelength being measured, and is amplified by either the optical or the electronic amplification system.

The wavelength is controlled by the right hand dial (c), which is graduated in arbitrary units. The calibration of this dial varies with room temperature and for precision work is redetermined at each point each time the machine is used. The approximate relation is given by the calibration curve.

The intensity of radiation is controlled by the width of the slit opening, which is set by the micrometer screw (B). This slit width should be kept as narrow as possible for exploration of spectra, but this is not as important in routine work.

II. Optical Amplifier

The current from the thermocouple passes to a sensitive galvanometer, enclosed in a cabinet to minimize variations in illumination. The galvanometer reflects a light beam on to a photocell the position of the beam being dependent on the deflection of the galvanometer. In operation,

a change in the voltage from the thermocouple produces a proportional change in the area of the photo-cell illuminated, and a consequent proportional change in the current output from the photo-cell. This current passes through a potentiometer (dial marked A on the control panel), where the desired amplification is set, and from there to a second galvanometer. The second galvanometer reflects a light beam to an illuminated scale, where the deflection is actually read.

III. Electronic Amplifier

In the electronic amplifier, a few microvolts, (direct current), from the thermocouple are impressed across a breaker, similar to a distributor, and are there thus synchronously converted to alternating current. This resulting A.C. voltage is amplified between 100,000 and 10,000,000 times in an amplifier of conventional design, and is then rectified by a second breaker synchronized with the first. A filter choke network installed inside the recording potentiometer smooths out irregularities in the resulting direct potential, which is then recorded by the potentiometer.

All the controls for the electronic amplifier are on the front panel of the amplifier unit itself. The degree of amplification is controlled by the "Gain" dial. The "Balance Coarse", and "Balance Fine" adjustments control the position of the zero trace on the recording potentiometer. The "Test Microvolts" dial injects a known voltage at the input, for testing amplification. The amplifier is connected to a separate power supply. Both must be supplied with regulated 117 volt alternating current.

IV. Control Panel

Degree of amplification and the positions of light spots are set by the control panel. Dial 1 is an eleven-point switch; which, by means of small impressed voltages, regulates the position of the light spot on the photocell. Dials 2 and 4 both set the position of the light spot on the illuminated scale, in a similar manner. Dial 3 (also marked A) controls the amplification of the optical amplifier.

Connections to the control panel are through plugs from the other units, marked to match sockets behind the panel. For routine operation, using the optical amplifier, turn both switches on the control panel upward. For operation with the electronic amplifier, turn both switches downward. These switches automatically connect the proper units. For operation of the recording potentiometer off the optical amplifier, turn both switches up and replace plug No. 4, from the second galvanometer, with the plug from the potentiometer. For this type of operation, the extra filter unit installed by the Perkin-Elmer Corporation in the lower left corner of the potentiometer is disconnected at the potentiometer terminals marked -T and C⊬. Connect the line from the control panel at these terminals, the green wire to C⊬ and the yellow wire to -T.

V. Batteries

The automobile headlight used in the optical amplifier unit, inclosed in the cabinet, is supplied with 6 volts direct current from either of two storage batteries, numbered 1 and 2. A double pole, double throw switch N

-4-

between the spectrometer and the A- frame draws current for the light from battery 1 or battery 2, as marked by the switch. When not using the light, turn the switch to its central position, which is the "off" position.

The batteries are charged by a battery charger on the table behind the operator. The battery to be charged is selected by a switch P. One battery should be charging at all times. Never draw current from a battery attached to the charger or other batteries.

When starting up the spectrometer, note, by the setting of switch P, which battery is being charged. Connect the other battery to the light by switch N. When shutting down, set the switch N to the neutral position, and flip switch P over, to charge the battery which has just been used.

It is, of course, necessary to add distilled water to the batteries from time to time.

VI. Routine Operation Using Optical Amplifier

1. Open water valve (D) one-sixth turn.

2. Make sure that water is flowing out the drain before connecting the electric lines. If the water is turned on too far, the rubber tubing may break and perhaps seriously damage the salt windows or other parts of the spectrometer.

3. The electric plugs are marked by the following code:

F: scale illuminating lamp

G: battery charger and gas analyzer

-5-

H: Brown potentiometer

K: Motor drive for spectrometer

L: Variac to Globar

M: Electronic amplifier

Plug G is not directly concerned with the operation of the spectrometer, and is kept connected at all times. Plug L, the power source for the Globar, is always connected when setting the apparatus in operation. For routine operations, connect plug F also.

4. Set the variac to give 250-300 watts. The number of watts is the product of volts times amperes as read on the meters. The proper setting is usually near 50-70 volts and 6-4 amperes.

5. Switch on the control panel.

6. Throw switch N to connect the battery <u>which has not been charging,</u> as indicated at switch P.

7. Open the door of the cabinet.

8. With the spectrometer shutter closed, and the slit set at approximately the setting to be used, adjust the position of the light spots on the photoelectric cell by means of switch 1 on the control panel until the light spots cover about 1/16 inch at the right hand edge of each of the sensitive (dark) areas of the photocell.
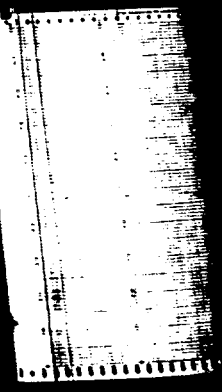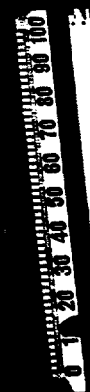
9. Set the wavelength dial C at the approximate setting to be used.

10. Open the shutter.

11. The light spots on the photocell will swing to the left. If they swing so far that the right hand edges of the sensitive areas are left dark, it will be necessary to cut down on the slit width (B).

12. Close the cabinet.

13. If the wavelength dial will not turn, it is because the clutch, connecting the motor drive to the spectrometer, is connected. To disengage the clutch, pull the sleeve W forward, toward the spectrometer.

14. By means of dial 2 or 4, set the light spot in the graduated scale "S" near the zero point (at the left end of the scale).

15. Adjust the amplification dial to give the desired deflection.

16. In about 15 to 20 minutes from the time it is first switched on, the spectromet. is ready for use.

17. From time to time, open the cabinet to check the position of the light spots with the shutter both open and closed, and adjust switch 1 as necessary. More often, it will be necessary to readjust the zero position of the light spot on the illuminated scale. This may best be accomplished by turning knob T below the illuminated scale. When this does not give adequate correction, adjust dials 2 and 4.

18. To shut down the spectrometer, pull out plugs L and F, leaving G, of course, in.

19. Turn off the water valve D.

20. Turn off the switches on the control panel.

21. Set the double-pole, double-throw switch N at its center position.

22. Flip the battery charging switch P over to charge the battery which has been used.

23. Adjust, if necessary, the variac supplying voltage to the charger, to keep the charging rate low enough.

CONTROL PANEL

SCALE "S"

SPECTROMETER

ELECTRONIC AMPLIFIER

CABINET (OPTICAL AMPLIFIER)

RECORDING POTENTIOMETER

7.7

7.7

FIGURE 2
SPECTROMETER
UNIT

7.7

PHOTO CELL

53523
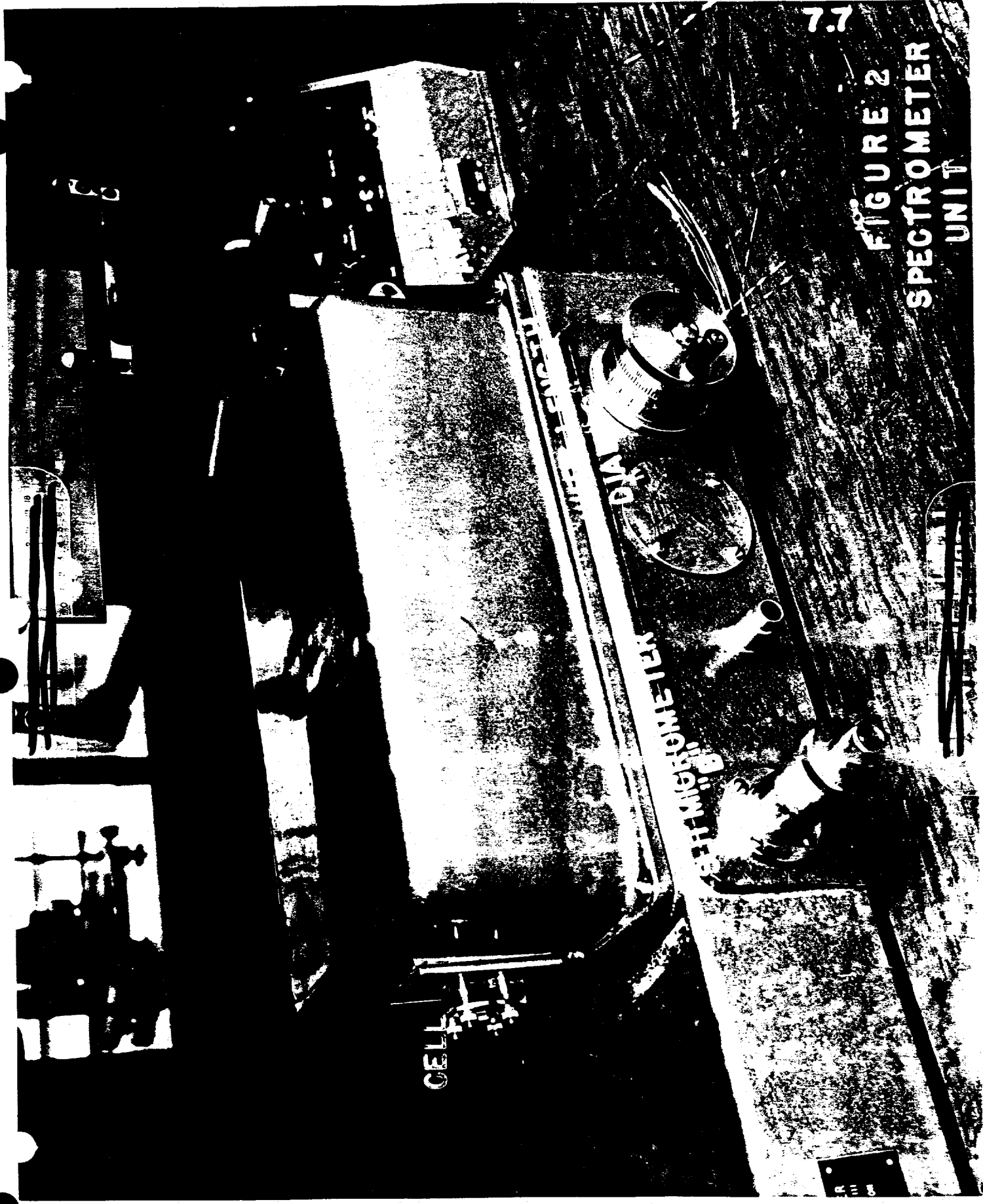
FIGURE 3
OPTICAL
AMPLIFIER
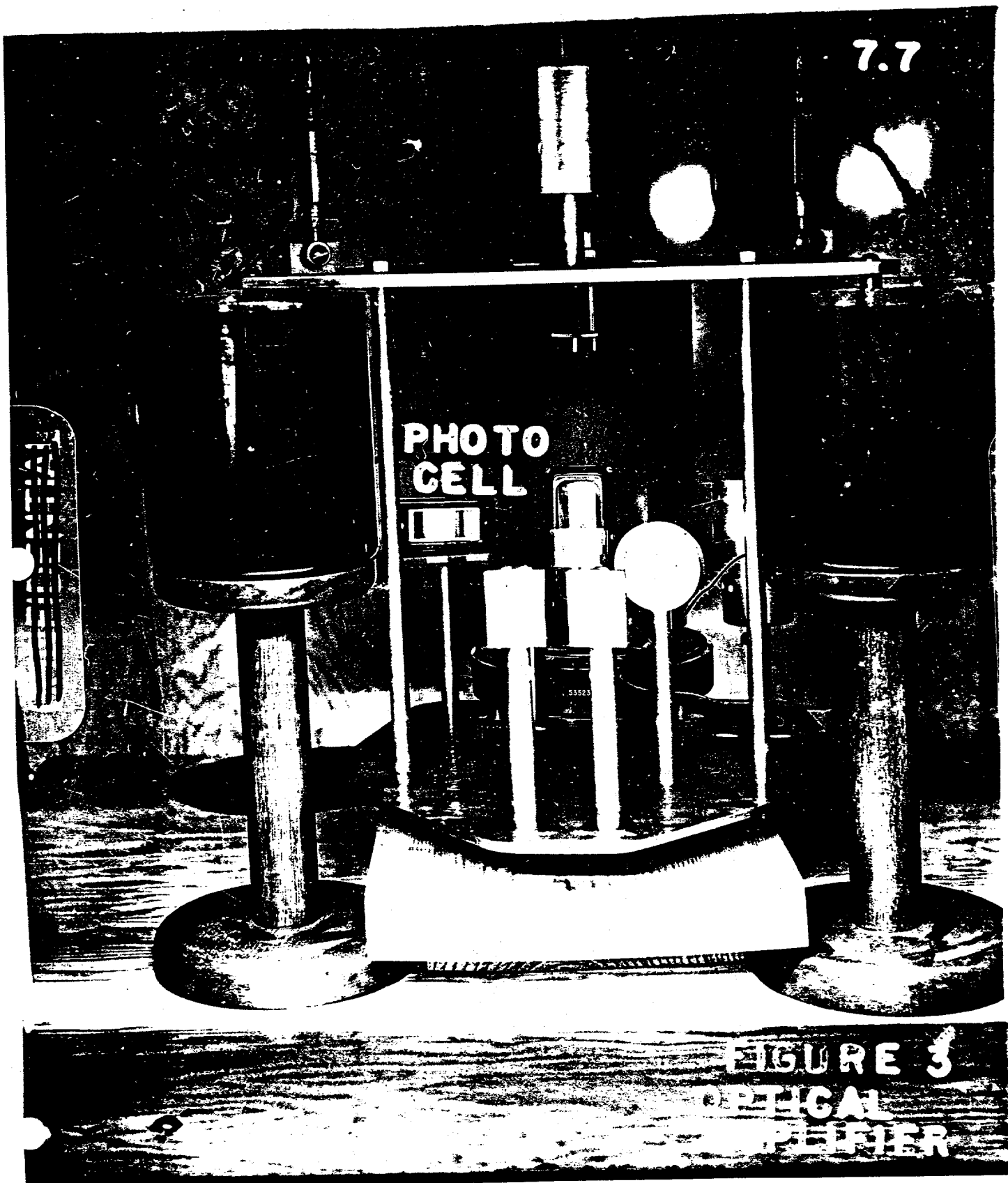
FIGURE 4
MOTOR DRIVE FOR
WAVE LENGTH DIAL

OPERATION OF THE HELLIGE TURBIDIMETER

The Hellige turbidimeter is used to determine the turbidity, expressed as parts per million of SiO_2, of the filtered (or sanitary) water both before and after filtering, and in the water rinse tanks used in the cleaning area. The operation of the Hellige instrument is very simple if the following procedure is followed:

1. Snap the switch on the left hand side of the instrument case to the "ON" position.

2. Rinse the clear glass cup with the water to be tested and fill to the mark etched on the side of the cup.

3. Insert the ground glass (constant level) cup, and place the ensemble in the space provided on the platform within the instrument.

4. By means of the dial knob on the right hand side of the instrument case and by observing through the eyepiece, adjust the small inner circle in the field until it has the same appearance as the large circular field that encloses it.

5. When the adjustment has been completed, read the number on the dial opposite the white line on the case. Record this number on the report sheet.

6. When making the final report, the calibration curve for the instrument should be used to convert the scale reading (recorded as noted above) to parts per million SiO_2.

GRAPH FOR HELLIGE TURBIDIMETER

SERIAL NO.   460

BULB   B

TUBE   20 MM

FILTER   NONE

TURBIDITY (PARTS PER MILLION SiO₂)

130

100

50

SCALE READINGS

50   100
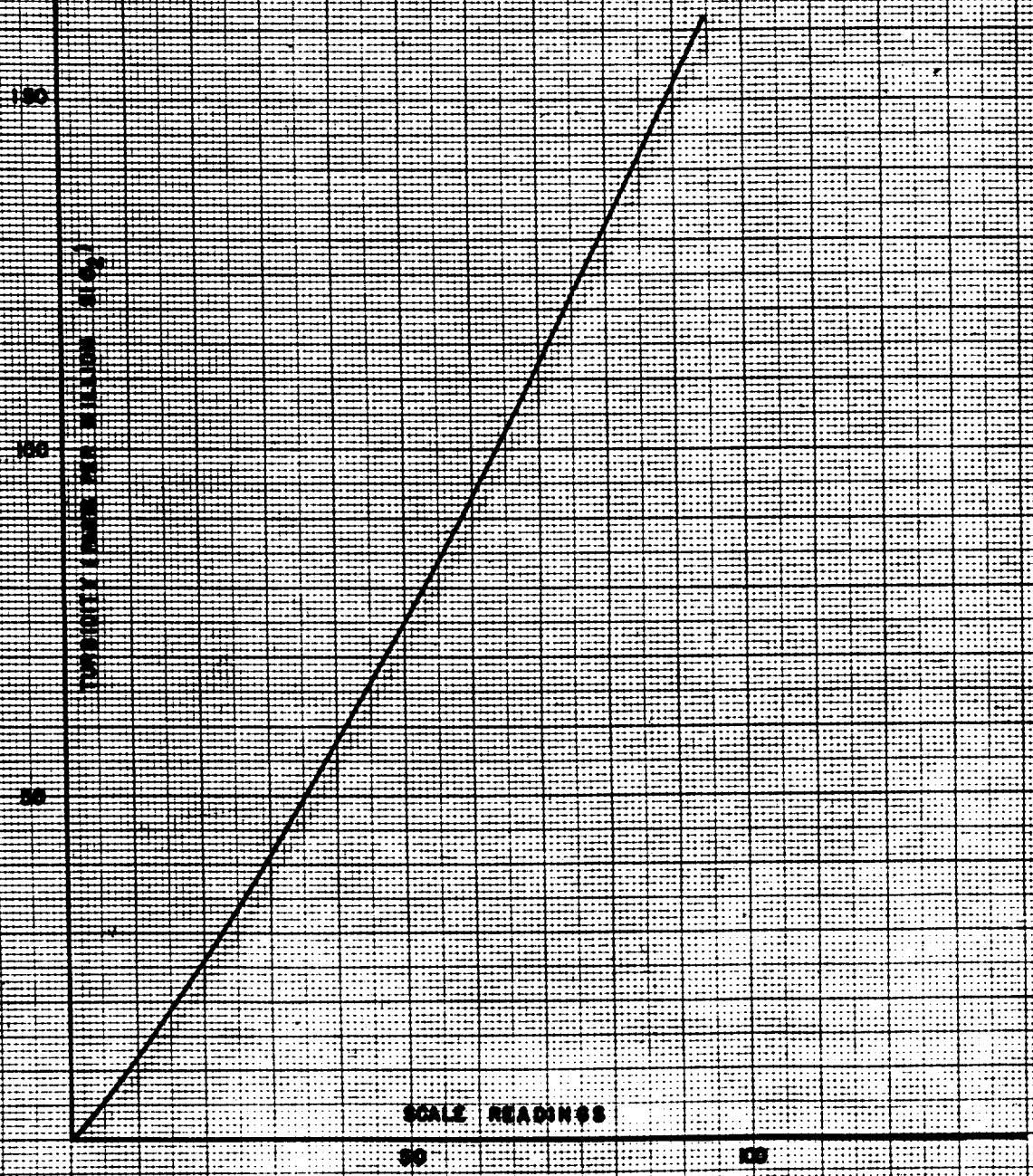
OPERATION OF THE BECKMAN INDUSTRIAL pH METER

The Beckman Industrial pH meter is used in this laboratory for the determination of pH of water samples and in one acid determination. The operation of the meter is very simple if the directions given here are carefully followed.

(1) Adjustment of the Meter.

With the rubber cap removed from the end of the calomel electrode, mount the electrodes in their holder so that the calomel electrode projects slightly lower than the glass electrode. Be sure they cannot touch the bottom of the beaker when the holder is lowered against its stop. Remove stopper from calomel electrode during use.

With control knob in the "OFF" position, the meter should read exactly 7 pH. Adjust, if necessary by turning the screw below the meter scale.

With push button in lower right hand corner in up position, turn switch to "ON" and leave in this position a few seconds.

Turn switch to 7-14 range and adjust meter to 7 pH using Amplifier Control Knob in lower left hand corner. Turn switch to 0-7 range and adjust to 7 pH with STD knob. Check the amplifier adjustment occasionally during use.

Immerse electrodes in a buffer solution of known pH. Place switch on proper range, press button, and adjust meter to buffer pH by means of AP knob. The meter is now ready for use in pH determinations.

(2) Use of the meter.

To determine pH of test solution, clean electrodes, immerse in test solution and select a pH range by means of the control knob (either 0-7 or 7-14). Press button. The meter will indicate the pH automatically.

If the needle goes off scale, turn switch to other range. If a continuous indication is desired, as in titration, lock the push button down. Release occasionally to check amplifier adjustment.

Instructions for use and operation of the L & N pH meter are given on the inside cover of the case for that instrument.

<u>DETERMINATION OF ALUMINUM IN C-616</u>

<u>Method:</u>

Aluminum, in ammonium buffered solution, reacts with aluminon to form a red lake whose intensity is measured colorimetrically. Beryllium, chromium and iron form lakes that interfere.

<u>Reagents and Apparatus:</u>

1. Beckman spectrophotometer or other suitable colorimeter.

2. pH meter.

3. Aluminon solution – Dissolve 2.0 grams of aurin-tricarboxylic acid in a minimum quantity of ammonium hydroxide. Dilute with water to 1 liter.

4. Acetone, c.p.

5. Acetone solution, 20 per cent.

6. Glacial acetic acid.

7. Hydrochloric acid, concentrated.

8. Ammonium acetate.

9. Ammonium carbonate.

10. Ammonium hydroxide, concentrated.

<u>Procedure:</u>

1. Add 5 ml. of concentrated hydrochloric acid and 5 ml. of glacial acetic acid to 20 to 25 ml. of sample solution of known T content. (The sample is prepared by hydrolyzing C-616 as in Procedure 2.3.) (Determination of T in C-616 Assay Samples, Part A. A portion of the diluted T-sulfate solution obtained in Step 8, Part A of the latter procedure is taken as a sample for this determination.)

2. Add 1.5 grams of ammonium acetate. Stir until salt dissolves.

3. Add 20 ml. of c.p. acetone and 5 ml. of 0.2 per cent aluminon solution. Stir.

4. Add solid ammonium carbonate until the pH of the solution is between 4 and 5. Allow to stand 15 minutes to obtain full color development.

5. Neutralize with ammonium hydroxide to pH = 7.00 and dilute to 100 ml. in a volumetric flask with 20 per cent acetone solution.

6. Prepare a "blank" by adding the reagents to an aluminum-free T solution as in Steps 1 to 5 above. (See Note (3)).

7. Determine the transmission of the sample at 450 millimicrons with the spectrophotometer against the "blank" prepared in Step 6 above.

8. Calculate the aluminum content of the sample by means of a calibration curve previously obtained with samples of T solution containing known amounts of aluminum. (See note (3)).

Calculations:

$$\text{Mg. T in sample} \times \frac{352}{238} = \text{mg. C-616 in sample}$$

$$\frac{\text{Mg. aluminum in sample}}{\text{Mg. C-616 in sample}} \times 100 = \text{per cent aluminum in C-616}$$

Notes:

1. All equipment except the spectrophotometer cells should be cleaned with chromic acid solution and thoroughly rinsed with distilled water.

2. The volumetric flasks should be rinsed with acetone. This appears to prevent precipitation of the complex.

3. The concentration of T in the solutions compared should be of the same order. However, this has not been found to be critical over a wide range.

DETERMINATION OF BORON IN C-616

Method:

The boron is separated from the other elements by distillation as methyl borate, $(CH_3O)_3$ B. The ester is distilled into an alkaline solution in which it is hydrolyzed. The hydrolyzed distillate is evaporated. An alcoholic solution of curcumin together with a mixture of oxalic and hydrochloric acids is added. The red color formed with curcumin and boron is developed and measured colorimetrically.

(Reproducibility is very good provided extreme caution is taken to prevent contamination and duplicate runs are made as nearly alike as possible. Volumes, weight, time factors etc. mentioned in the ensuing procedure are not all critical. Some of them are. The others will serve as practical limits and should be followed closely. It is essential that the same lots of reagents be used both in establishing the calibration curve and in the actual determinations.)

Reagents and Apparatus:

1. Oxalic-hydrochloric acid mixture - Prepare as follows:

    20 milliliters distilled water

    20 milliliters c.p. ethanol

    5 milliliters concentrated hydrochloric acid

    4 grams oxalic acid

2. Curcumin extract - Dissolve 0.10 grams of crystalline curcumin in 100 ml. of c.p. ethanol.

3. Methanol, c.p.

4. Sodium carbon solution - (0.2N).

5. Ammonium hydroxide, c.p., boron-free.

6. Concentrated sulfuric acid.

7. Platinum evaporating dishes, approximately 150 ml. capacity.

8. Platinum trap with adapter to fit a "Hoke" sample tube.

9. Water bath, regulated to 55° C. $\angle 2^\circ$ C.

10. Distillation and reflux apparatus made of boron - free glass.

11. Beckman spectrophotometer.

Procedure:

A. Sampling Procedure: (references are to Figure 1)

1. The sample (C-616 is contained in a "Hoke" tube (A). (Glass sampling tubes should not be used as they may contain boron.) Fit the "Hoke" tube with an adapter (E) and connect to a platinum trap (B), the lower part of which is immersed in liquid nitrogen (C).

2. Connect the exit side of the trap to an aspirator and evacuate the system to a pressure of 20 inches of mercury.

3. Open the valve on the "Hoke" tube and distill the C-616 for ten minutes. It may be necessary to heat the Hoke tube gently, starting near the rubber connection (F) on the copper tube working down to the bottom of the Hoke tube.

4. Hydrolyze the C-616 in the trap by adding water and wash the contents from the trap into a platinum dish. This solution should contain 500-800 mg. of TO_2F_2.

B. Distillation Procedure: (See Figure 3 for Apparatus)

1. Add 0.5 ml. concentrated sulfuric acid to the C-616 sample in the platinum dish. Evaporate on a steam bath until TO_2SO_4 crystallizes freely.

2. Dilute to approximately 25 ml. Take a small aliquot, (1 ml. usually) and analyze colorimetrically for T.

3. Pipette an aliquot containing 150 to 200 mg. T into the reaction flask (H). Add boron-free ammonium hydroxide until the first permanent precipitate forms. Dissolve the precipitate by adding concentrated sulfuric acid dropwise; then add two drops more.

4. Pour 5 ml. of 0.2 N sodium carbonate into the soft glass receiving bottle (K) but do not stopper tightly. (The sodium carbonate solution is stored in lucite ware.)

5. Add 25-30 ml. of c.p. methanol to the solution in the reaction flask; and attach reflux condenser (D) immediately. Reflux vigorously for an hour.

6. At the end of the refluxing period, stopper the receiving bottle tightly and adjust the aspirator to give a pressure of 20 inches of mercury. Remove the reflux unit (Figure 2). Wash it immediately with methanol, and replace it with the boron free glass tube (M) drawn to a capillary. Readjust the aspirator so as to give from 2-4 bubbles per second through the T solution in the distilling flask.

7. Distill 200 ml. into the receiving bottle by keeping the water bath at 93-98° C. (incipient boiling). Add 10-15 ml. of methanol periodically. Do not let the volume in the reaction flask (H) fall below 15 ml.

8. Evaporate the distillate to dryness on a steam bath to avoid spattering. Use a 150 ml. porcelain evaporating dish. (The analysis may be safely interrupted and the samples may be stored at this point.)

C. Procedure for Development of the Boron - Curcumin Color:

1. Dissolve the evaporated distillate in 2 ml. of the oxalic-hydrochloric acid mixture, rotating the dish to bring the residue into solution completely.

2. Add 3 ml. of 0.10 per cent curcumin extract.

3. Float the evaporating dish on the surface of constant temperature water bath (55° C. $\angle 2^{\circ}$ C.) for exactly one hour to develop the color.

4. Extract the red boron complex with c.p. ethanol and filter through a No. 41 Whatman filter paper into a 25 ml. volumetric flask. Dilute to volume with c.p. ethanol.

5. Measure the transmission of this solution with a Beckman Spectrophotometer using a 1 cm. cell and a wavelength of 540 millimicrons. Ethanol is used as the 100 per cent transmission standard.

6. Determine the amount of boron from a calibration curve obtained by developing the boron-curcumin color with known quantities of boron. (Use a boric acid solution containing one microgram of boron per ml. for determining the calibration curve points. Evaporate the aliquots to dryness with 5 ml. of 0.2 N sodium carbonate. Proceed to develop the red boron color as in Steps 1 to 5 above.)

7. Check the purity of the reagents by a blank determination carrying it through the distillation procedure and the color development procedure as given above.

8. Subtract the average blank value from the value obtained for the sample in Step 6 above.

Calculations:

1. Mg. T in sample x $\frac{352}{238}$ = mg. C-616 in sample.

2. $\frac{\text{Mg. boron in sample}}{\text{Mg. C-616 in sample}}$ x 100 = per cent boron in C-616

Note: A typical calibration curve for boron curcumin complex is given.

A· HOKE TUBE

B· PLATINUM TRAP

FIGURE I

SAMPLING APPARATUS

COLD WATER INLET

BORON FREE GLASS
(10 OR 12 MM O.D.)

D - REFLUX UNIT

20 CM
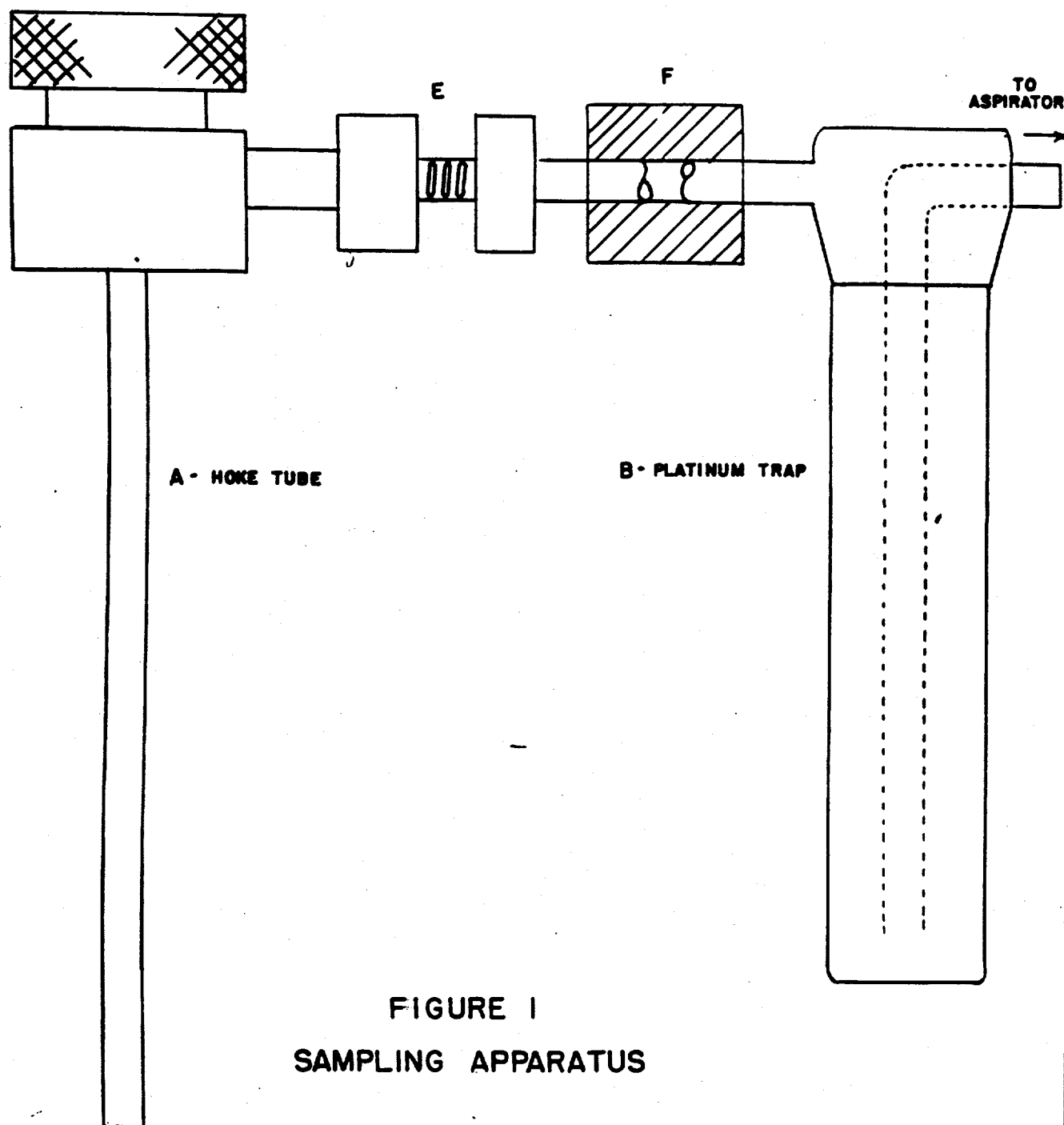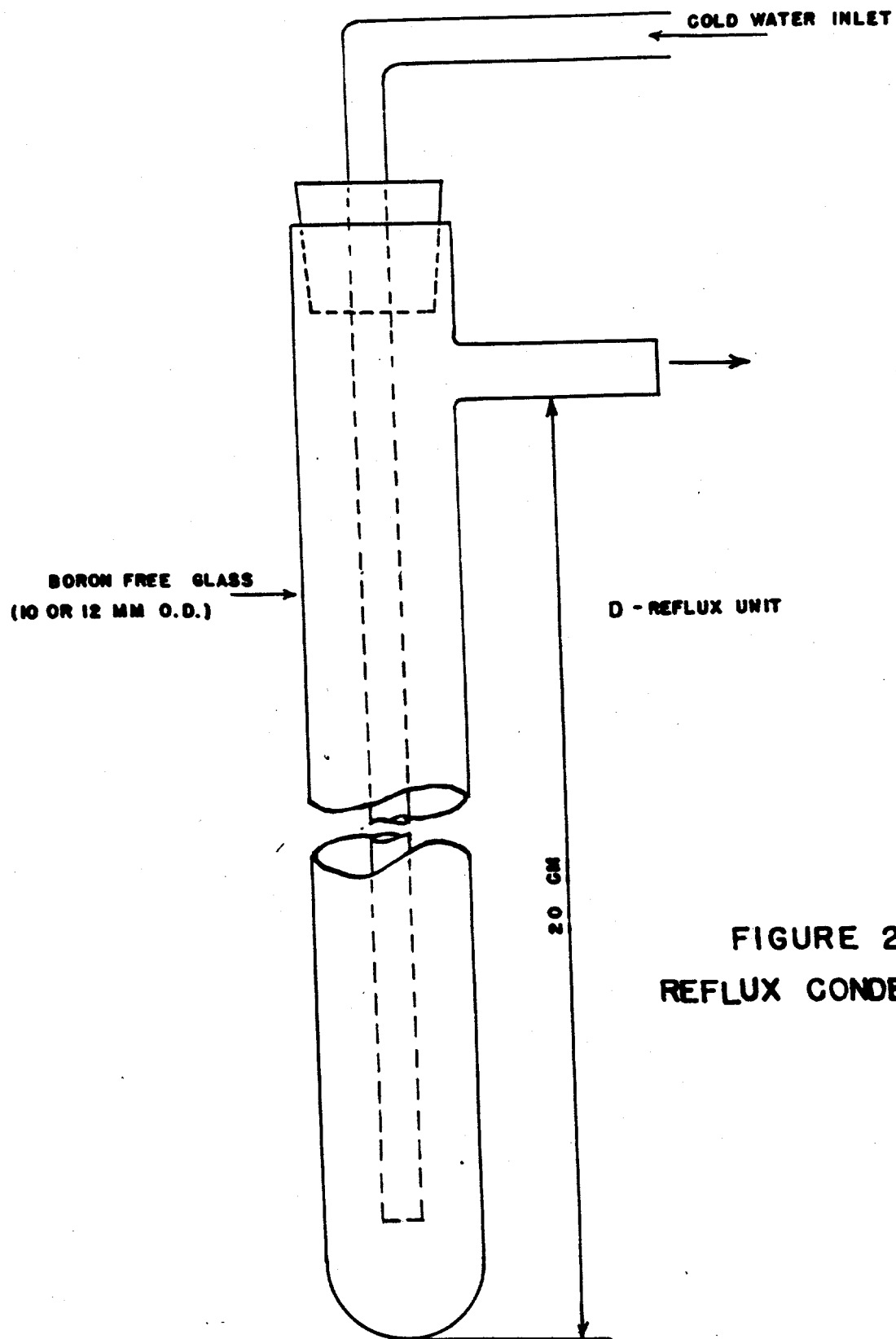
FIGURE 2
REFLUX CONDENSER

GLASS WOOL
AIR FILTER

SEPARATORY FUNNEL
150 ML

BORON FREE GLASS
INLET TUBE - M

VYCOR DISTILLING
FLASK - H

CONDENSER
20 CM - J

TO ASPIRATOR

SOFT GLASS
BOTTLE - K

SINTERED GLASS PLATE - L
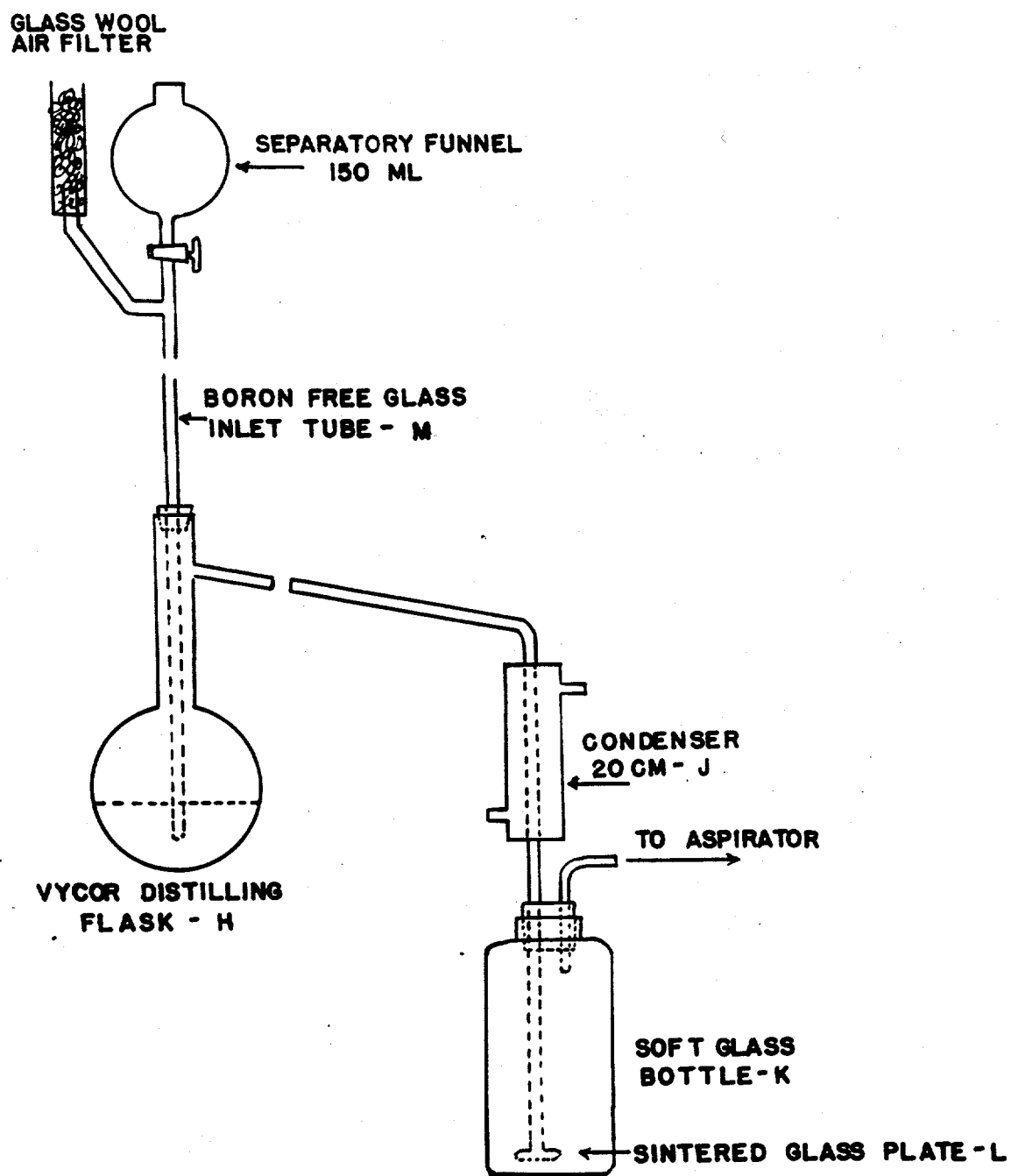
FIGURE 3

DISTILLATION APPARATUS

CALIBRATION CURVE FOR BORON CURCUMIN COMPLEX
SAMPLE VOLUME - 25 ML
LIGHT PATH - 1 CM
WAVE LENGTH - 540 MILLIMICRONS

PERCENT TRANSMISSION

MICROGRAMS OF BORON
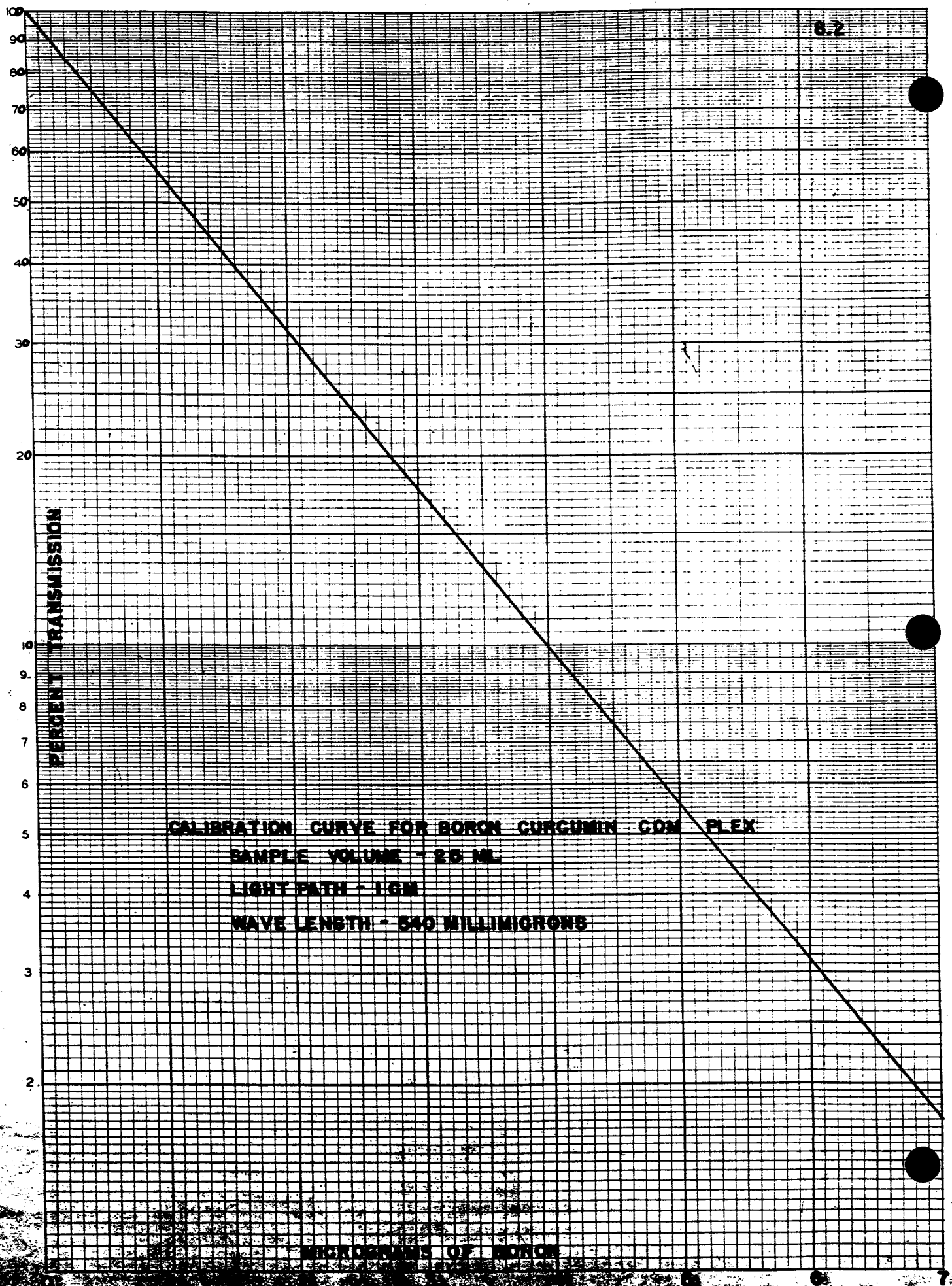
DETERMINATION OF MOLYBDENUM IN C-616

Part A - Colorimetric

Method:

The thiocyanate complex of molybdenum is formed, extracted from interfering ions with normal butyl acetate and measured colorimetrically on a Beckman spectrophotometer at a wavelength of 470 millimicrons.

Reagents and Apparatus:

1. Sodium peroxide solution, 5 per cent - dissolve 25 grams of c.p. sodium peroxide (Parr) in 300-400 ml. of water. Filter through a glass frit. Dilute to 500 ml. Do not use after seven days.

2. Normal butyl acetate.

3. Ammonium thiocyanate solution - dissolve 20 grams of ammonium thiocyanate in 100 ml. of distilled water.

4. Stannous chloride solution - dissolve 350 grams of stannous chloride in 1:1 hydrochloric acid and add a few pieces of tin or approximately 15 ml. of oil to prevent oxidation by the air which results in the solution becoming cloudy.

5. Beckman spectrophotometer.

Procedure:

A. Sampling

In Figure I, (A) is an ID or Harshaw type container for C-616. (B) (C) and (D) are 500 ml. Erlenmeyer flasks. Flasks (C) and (D) contain approximately 150-175 ml. of water.

1. Close all valves in the apparatus. Connect the sample bomb (A) to the sampling train.

2. Evacuate the system by means of an aspirator.

3. Heat the copper tube between (A) and (B) to 70°-80° C.

4. Heat the valve and neck of the cylinder (A) to approximately 50° C. in order to vaporize any C-616 which may have solidified there.

5. Open the valve on cylinder (A) carefully. (If the lines are unblocked and the pressure in the system is correct the flask (B) will be filled with C-616 fog).

6. Close the valve at (A) after 10-15 seconds, and open and close valve (B) rapidly in order to purge trapped C-616 from the copper tube between (A) and (B). If necessary shake flask (B) to wash its walls.

7. Repeat Steps 5 and 6 approximately 5 times until an appropriate quantity (2 to 5 gram of T) of C-616 is dissolved in the flask (B).

8. When an adequate s mple has been obtained and before opening the valve at B, open the valve at (D). Water from flask (C) will flow into (B) and rinse the line from (B) to (C). To stop flow open the valve at (B). Do not allow the volume of solution in flask (B) to exceed 150 ml.

NOTE: The heating of the line between (A) and (B) must be maintained. If the flow of C-616 does not proceed evenly when the line is unblocked, heat the valve and lines leading from cylinder A) with caution.

B. Preparation of Sample:

1. Transfer the sample solution to a platinum dish. (It may be necessary to evaporate some of the water to accommodate all of the solution if the dish is small.)

2. Add 10 ml. of concentrated sulfuric acid and evaporate until copious fumes of SO_3 are produced.

3. Add 60 ml. of water and warm to dissolve. The TO_2SO_4 dissolves slowly.

4. Filter the solution through a Whatman No. 42 filter paper. Silica is removed in this step.

5. Collect the filtrate in a 100 ml. volumetric flask.

6. Dilute the filtrate to volume with water.

7. Determine the T concentration of the diluted solution colorimetrically by the Sodium Peroxide Method (See Procedure 6.2).

C. Extraction of the Molybdenum Complex:

1. Take an aliquot (containing two grams of T) of the solution prepared above.

2. Pour the aliquot into a 100 ml. graduated cylinder. Dilute with distilled water to the 70 ml. mark on the cylinder (Note: If the aliquot is larger than 70 ml. first evaporate the sample to the proper concentration range).

3. Cool the reagents to be used in ice water, i.e. the solutions of ammonium thiocyanate, stannous chloride, and n-butyl acetate.

4. Cool the 70 ml. sample from (2) for five minutes in ice water and transfer it to a 500 ml. separatory funnel.

5. Add 2 ml. of 20 per cent ammonium thiocyanate (cold) and shake two or three times.

6. Add 5 ml. of stannous chloride (35 per cent) and shake two or three times.

7. Add 25 ml. of n-butyl acetate and shake 60 to 80 times with vigor.

8. When the layers are separated (2-5 minutes), drain and discard the aqueous layer.

9. Add 50 ml. of cold 10 per cent sulfuric acid, 2 ml. of 20 per cent ammonium thiocyanate and 2 ml. of 35 per cent stannous chloride solution and shake 60-80 times vigorously. (Note: Cool these solutions in ice water as before).

10. When the layers are separated, drain and discard the water layer. Iron, which interferes with the determination is removed in the aqueous layer.

11. Filter the n-butyl acetate layer through <u>dry</u> number 41 Whatman filter paper into a clean* dry 30 ml. glass stoppered bottle.

12. Determine the transmission with a Beckman spectrophotometer at 470 millimicrons, using molybdenum-free T sulfate as standard and determine the amount of molybdenum present from a calibration curve determined similarly.

---

*The funnel and bottles must be cleaned with 1:1 hydrochloric acid and distilled water, then alcohol and finally dried in the oven. Extreme care must be taken to keep these free from iron.

Calculations:

$$\frac{\text{Micrograms of Mo found}}{\text{Sample weight in grams**}} = \text{P.p.m. Mo in sample}$$

P.p.m. of Mo x 2.18 = p.p.m. MoF_6

One p.p.m. of MoF_6 = 0.0001 per cent MoF_6

**Sample weight of 2 grams is used.
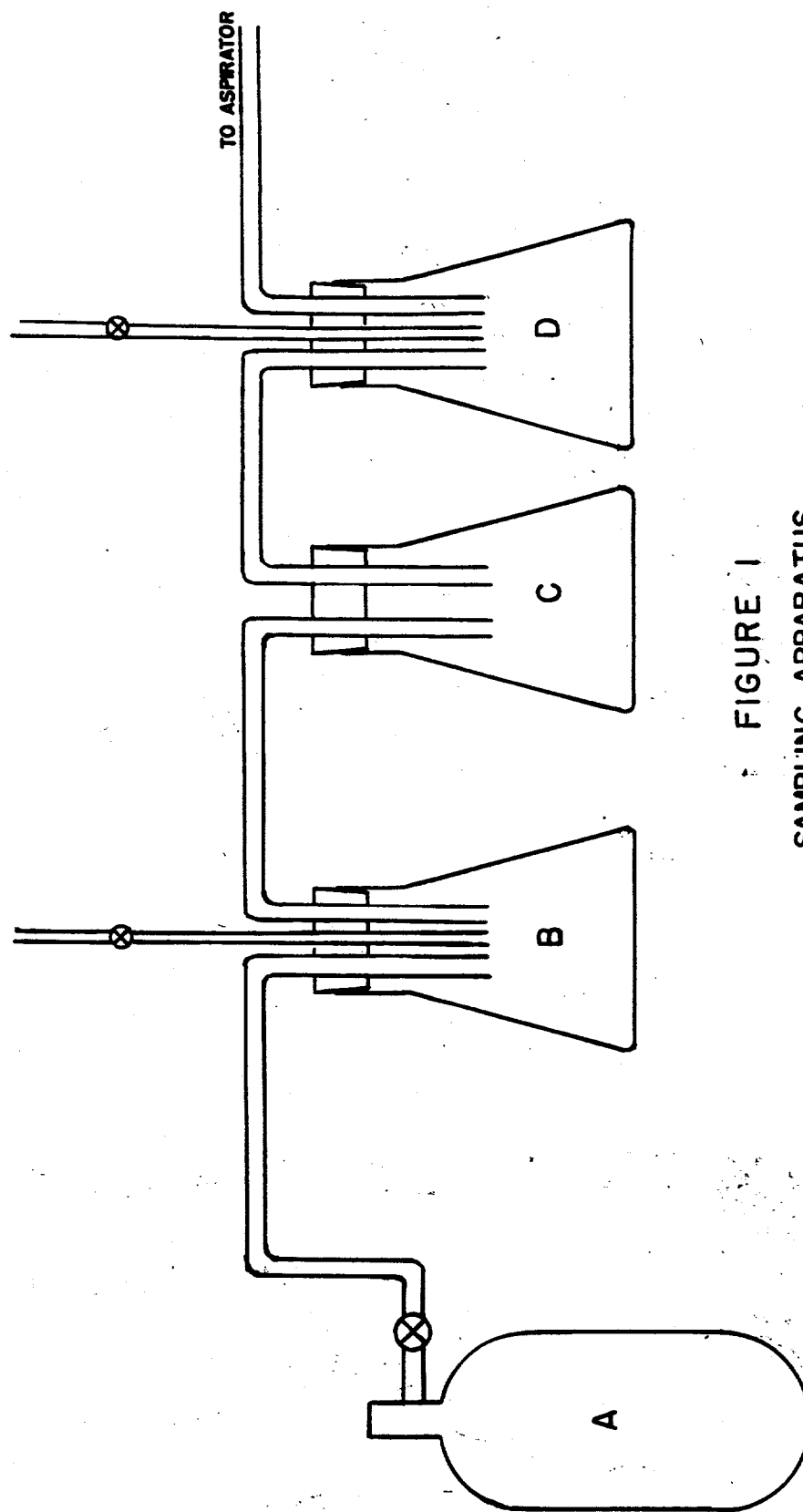
FIGURE 1

SAMPLING APPARATUS
FOR
DETERMINATION OF MOLYBDENUM
IN C-616

TO ASPIRATOR

8.3

A SPECTROGRAPHIC METHOD FOR THE DETERMINATION

OF MOLYBDENUM IN 616

Method

The 616 is transferred under vacuum to a pyrex glass tube cooled in liquid nitrogen, hydrolyzed with water, and evaporated to dryness in a platinum evaporating dish. A weighed portion of the dry material (TO_2F_2) is converted to the sulfate, dissolved in water and made to a definite volume, copper added and a sulfide precipitation of molybdenum in copper made in a solution 0.3 normal with respect to sulfuric acid. The sulfides are separated from the solution, washed with 0.3 normal sulfuric acid with the aid of a centrifuge, dried overnight in a drying oven, transferred to graphite electrodes, and heated, first, gently to remove the excess sulfuric acid, then more strongly to convert the sulfides to oxides. The material is finally burned in a D. C. arc, the spectra photographed, and the molybdenum determined by comparison of the sample spectrum with spectra from standard samples having known amounts of molybdenum in them.

Reagents and Apparatus

1. TO_3 dissolved in sulfuric acid, 1.625 grams of TO_3 dissolved in 10 ml. of sulfuric acid and diluted to 200 ml. 10 ml. of this solution is equivalent to 0.100 gram of TF_6.

2. $CuSO_4.5H_2O$ dissolved in water. 3.928 grams of copper sulfate dissolved in one liter of water. This solution contains 1 mg. of copper per ml.

3. Molybdenum metal powder dissolved in sulfuric acid (conc.) and diluted until its concentration is 1 microgram of Mo per ml.

-2-

4. Three normal sulfuric acid solution.

5. 0.3 normal sulfuric acid solution.

   NOTE: Reagents should be molybdenum free.

6. Standards used for 5 to 20 p.p.m. of Mo in TF$_6$.

   A. 0.100 gram of TF$_6$ plus 10 mg. of copper (Blank)

   B. 0.100 gram of TF$_6$ plus 10 mg. of copper plus 0.5 micrograms of Mo

   C. 0.100 gram of TF$_6$ plus 10 mg. of copper plus 1.0 micrograms of Mo

   D. 0.100 gram of TF$_6$ plus 10 mg. of copper plus 1.5 micrograms of Mo

   E. 0.100 gram of TF$_6$ plus 10 mg. of copper plus 2.0 micrograms of Mo

7. Standards used for 1 to 10 p.p.m. of Mo in TF$_6$.

   F. 0.100 gram of TF$_6$ plus 10 mg. of copper (Blank)

   G. 0.100 gram of TF$_6$ plus 10 mg. of copper plus 0.2 microgram of Mo

   H. 0.100 gram of TF$_6$ plus 10 mg. of copper plus 0.4 microgram of Mo

   I. 0.100 gram of TF$_6$ plus 10 mg. of copper plus 1.0 microgram of Mo

   J. 0.100 gram of TF$_6$ plus 10 mg. of copper plus 2.0 microgram of Mo

8. A Bausch and Lomb Spectrograph, large Littrow model with quartz optics.

9. Applied Research Laboratories rectified arc source.

10. Applied Research Laboratories Comparator.

11. Applied Research Laboratories Plate Developer.

12. Infra-red plate drier, built in this laboratory.

13. Electrode heater, built in this laboratory.

14. Centrifuge, built by International Equipment Co., Boston, Mass.

15. Applied Research Laboratories Electrode Cutter, (Modified at this Laboratory).

16. Platinum evaporating dishes, and platinum crucibles.

17. Pencil sharpener for pointing 1/8 inch graphite electrodes.

18. Spectrum analysis plates No. 1 (supplied by Eastman Company).

19. 1/8 and 1/4 inch special graphite spectroscopic electrodes.

20. Tank hydrogen sulfide.

21. D-19 developer (supplied by Eastman Company).

22. F-5 fixer (supplied by Eastman Company).

23. Molybdenum metal powder (supplied by A.D. MacKay of New York).

24. $TO_2(NO_3)_2 \cdot 6H_2O$ for making TO_3. Mallinckrodt Chemical Co.

Procedure

1. Prepare graphite electrodes in advance. Cut 1/4 inch graphite rod into 3/4 inch sections. Make a 1/16 inch depression in one end with a 3/16 inch drill, and a 1/8 inch tapered hole in the other end. Cut the 1/8 inch graphite rod into 1-1/4 inch lengths, and point one end of each piece with a pencil sharpener.

2. To determine Mo in the range of 5 to 20 p.p.m. use 0.100 gram of TF_6. The equivalent of this weight in TO_2F_2 is 0.0875 grams.

3. To determine Mo in the range of 1 to 10 p.p.m. use 0.200 gram of TF_6. The equivalent of this weight in TO_2F_2 is 0.1750 grams.

4. To determine Mo in the range of 0.1 to 1 p.p.m. use 2.000 grams of TF_6. The equivalent of this weight in TO_2F_2 is 1.750 gram.

5. Weigh the required amount of sample and put it in a small platinum evaporating dish.

6. Treat the sample with 2 ml. of concentrated sulfuric acid.

7. Evaporate off the excess acid. (Treatment removes fluorine from sample).

-4-

8. Dissolve sample in 17 ml. of water and transfer it to a 150 ml. beaker.

9. Add 10 ml. of copper sulfate solution (equivalent to 10 mg. of copper).

10. Neutralize the solution with ammonium hydroxide.

11. Make solution 0.3 normal using 3 normal sulfuric acid.

12. Heat the solution and precipitate the sulfides by passing H_2S through it for 15 minutes (hood).

13. Transfer the sample to 100 ml. pear shaped centrifuge tubes using 0.3 normal sulfuric acid to assist in the transfer.

14. Bring centrifuge tubes to constant weight (several are done at one time).

15. Separate the sulfides from the solution with a centrifuge, and wash the precipitates four times with 0.3 normal sulfuric acid.

16. Set the centrifuge tubes in a horizontal position in the drying oven overnight.

17. Transfer the dried sulfides of copper and molybdenum to shallow crater electrodes using a small spatula for the job.

18. Put the electrodes containing the samples in an electrode heater and heat at a low temperature until H_2SO_4 is driven off.

19. Heat electrode more strongly until sulfides are converted to oxides. The heating is always kept below a red heat.

20. Expose the samples under the conditions outlined below.

Exposure of Sample

1. Use 1/8 inch upper graphite electrode.

2. Use 1/4 inch lower graphite electrode which contains the sample.

3. The lower electrode is the anode.

4. Distance between electrodes in 5/32 inch.

5. Distance from slit to sample is 42.5 cm.

6. Distance from slit to auxiliary lens is 32.0 cm.

7. The arc image is focused on the slit.

8. The burn is made with a 10 ampere D. C. arc.

9. The slit width is 30 microns.

10. The slit length is 1 mm.

11. The smallest aperture is used in front of the collimating lens.

12. There is no preburn, the exposure begins with the striking of the arc.

13. Plate – Eastman Spectrum Analysis Plate No. 1.

14. Development – The plate is developed 5 minutes in D-19 at 20° C.

15. Short stop – The plate is put in the shortstop for 30 seconds.

16. Fixing – The plate is put in the fix F-5 for 5 minutes at 20° C.

17. Washing – The plate is washed one to two minutes.

18. Drying – The plate is dried for 1 minute on an infra-red heated drier.

19. Split the plate in two equal sections. The samples are on one section and the standards are on the other section of the plate.

20. Compare the samples with the standards on the comparator.

CLEANING PROCEDURES

I.   CLEANING URINE SAMPLE BOTTLES

A.   If bottle is dry:

1. Clean well with cleaning solution.   (WEAR RUBBER GLOVES WHEN USING CLEANING SOLUTION).

2. Rinse with warm tap water to remove cleaning solution.

3, Boil for 10 minutes with 10 per cent nitric acid.

4. Rinse with tap water three times.

5. Rinse with distilled water four times.

6. Dry in steam cabinet after draining excess water.

B. If bottle is wet:

1. Rinse with warm tap water then follow same procedure as for dry bottles.

C. Bottle Caps

1. Boil caps in 5-10 per cent sodium carbonate for 3-4 minutes.

II.   PROCEDURE FOR CLEANING METAL CYLINDERS

1. To each cylinder add 400 ml. of trisodium phosphate.

2. Fill with hot water and insert a steam line to the bottom.

3. Rinse out trisodium phosphate and steam for at least one hour.

4. Add 10 per cent HCl and allow to stand for 20 minutes.

5. Rinse and add a mixture containing 6 per cent HNO_3 and 6 per cent H_2SO_4 for five minutes.

6. Rinse and examine to determine if clean. If clean, dry in steam cabinet.

MICRO DETERMINATION OF T IN URINE AND IN AIR SAMPLES

BY FLUORESENCE

Method:

Hexavalent T salts, in a matrix of fused anhydrous sodium carbonate and sodium fluoride give a characteristic yellow-green fluoresence under ultra violet light. The intensity of fluoresence is proportional to the concentration of T in the matrix. The intensity of fluoresence is estimated visually by comparison with a series of standards.

Reagents and Apparatus:

1. Anhydrous sodium carbonate, analytical grade, T^- free.

2. Sodium fluoride, analytical grade, T free.

3. TO_2 acetate standard solution, 1 mg. T per liter.

4. Glacial acetic acid.

5. Hydrochloric acid solution. One part acid in five parts distilled water by volume.

6. Twenty ml. platinum crucibles, low form.

7. One platinum cover (to fit twenty ml. crucible) for every six crucibles in use.

8. Five ml. porcelain crucibles, low form.

9. Hanovia Chemical and Mfg. Co. Ultra Violet light source, equipped with Hanovia bulb E-H4 and visible light filter.

10. Muffle furnace.

11. Hot plate with asbestos pad.

Procedure:

A. Preparation of fusion mixture: (200 gram quantity)

1. Clean a mortar and pestle thoroughly with chromic acid cleaning solution, followed by copious washing with tap and distilled water. Oven dry.

2. Weigh out 20.0 gms. sodium fluoride and 180.0 gms. anhydrous sodium carbonate.

3. Grind the above thoroughly in the mortar. Make certain complete mixing is obtained. Caution: Avoid breathing the sodium fluoride dust.

4. Transfer the mixture to a clean glass stoppered bottle. Seal with wax if not to be used immediately.

B. Preparation of Standards: (0.000, 0.025, 0.05, 0.15, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0, and 6.0 micrograms T).

1. Dissolve 89.1 mg. TO_2 acetate (dihydrate) in 20 ml. glacial acetic acid and dilute to one liter. (This is a stable solution containing 50.0 mg. T/liter).

2. Dilute two ml. of 50.0 mg. T/liter solution to 100 ml. (This 1 mg. T/liter solution must be prepared immediately before use.)

3. Measure the required volume of 1 mg. T/liter solution into clean platinum crucibles. Use a 5 ml. micro burette for this measurement.

4. Evaporate the solution to dryness on a hot plate.

5. Add 1.20 gms. of fusion mixture.

6. Fuse in muffle furnace at 800° C. for two minutes and forty seconds and pour a pellet. (See Part E). Note: New standard should be prepared weekly.

C. Standard Practice on air samples:

1. Pipette volume of liquid containing not more than four micrograms of T into platinum crucible.

2. Evaporate to dryness on hot plate.

3. When dry, add 1.20 gms. of fusion mixture.

4. Fuse in muffle furnace at 800° C. for two minutes and forty seconds and pour in a pellet. (See Part E.)

5. Compare the pellet with the standards. Comparison is made in a dark room under ultra violet light.

6. Report micrograms T per ml. solution analyzed.

D. Standard practice on urine samples:

1. Pipette two ml. urine sample into platinum crucible.

2. Evaporate to dryness on hot plate.

3. Ash in muffle furnace at 800° C. for two minutes and forty seconds.

4. Add 1.20 grams of fusion mix.

5. Fuse in muffle furnace at 800° C. for two minutes and forty seconds and pour a pellet.

6. Compare the pellet with the standards. Comparison is made in a dark room under ultra violet light.

7. Report micrograms T per ml. urine sample.

E. Pouring the pellet:

1. Place a clean platinum crucible cover in position not more than one foot from the furnace door.

2. Remove the crucible from the furnace and immediately pour the molten contents onto the clean cover. A pellet approximately 1/4 inch in diameter should be obtained.

F. Comparison of the sample pellet with the standards:

1. Place the standard pellets, round side up, in increasing order of T content, in 5 ml. porcelain crucibles glued to a 12" x 3" board.

2. Place the sample pellet, round side up, in a similar crucible.

3. With the sample and standards any convenient distance from the light source, move the sample along the series of standards until an approximate intensity match is found.

4. Move the sample and standards further away from the light source until the fluoresence of the sample is extinguished, and select the highest standard extinguished at this distance. This standard pellet contains the same amount of T as the sample. Note: The pellet will not fluoresce when hot, hence allow about 10 minutes between pouring the pellet and attempting a comparison.

G. Cleaning the platinum crucibles:

1. Place crucibles in a beaker and cover with 1:5 hydrochloric acid.

2. Place beaker on hot plate and let acid boil gently for at least five minutes.

3. Remove crucibles and wash copiously with tap water followed by distilled water.

4. Test each crucible by pouring a "blank" pellet before reusing.

SAMPLING FOR "T" COMPOUNDS IN THE ATMOSPHERE

Method:

Particles or gases containing T are collected in distilled water by means of a hand operated MSA Midget Impinger Pump and collection flask. The kinetic energy of the particles is momentarily reduced as they impinge on the bottom of the sampling flask. Wetting of the particle is thus enhanced and efficient collection results. The flask is designed so that by maintaining 12 inches of water vacuum in the pump, one cubic foot of air passes through the flask every ten minutes.

Reagents and Apparatus:

1. Chromic acid cleaning solution.

2. Distilled water.

3. M.S.A. Midget Impinger.

4. Impinger flask, 30 ml. with nozzle (see Figure 1).

Procedure:

A. Cleaning the flask

1. Clean flask and nozzle with chromic acid cleaning solution.

2. Rinse thoroughly with tap water four times.

3. Rinse thoroughly with distilled water four times.

B. Charging the flask:

1. Add distilled water to flask up to the 10 ml. mark.

2. Stopper flask by placing rubber cover first on the nozzle and then on the flask.

3. The bottom of the nozzle should be level with the lowest graduation on the outside of the flask.

-2-

C. Collecting the sample:

1. Remove the stopper on the flask and then the stopper on the nozzle.

2. Connect the rubber tube from impinger to the arm on the impinger flask.

3. Turn the crank on the impinger at a sufficient rate to maintain 12 inches of water vacuum measured by the gauge on the pump and at the same time probe the area to be sampled with the sampling flask.

    Note: At this rate of flow, one cubic foot of air will be sampled every ten minutes or approximately one fiftieth cubic meter of air will be sampled in seven minutes. Usually a 7 minute sample is taken. The crank may be turned in either direction. The rate of cranking is not critical over a large range. The most suitable rate may be determined after a few turns.

SAMPLING FOR "T" COMPOUNDS IN THE ATMOSPHERE

AIR INTAKE

AIR OUTLET

TUBE TO IMPINGER
ATTACHED HERE

NOZZLE

ML
30

25

20

15

10

5

IMPINGER FLASK
WITH NOZZLE
TWICE ACTUAL SIZE

COLLECTION
SOLUTION
10 ML
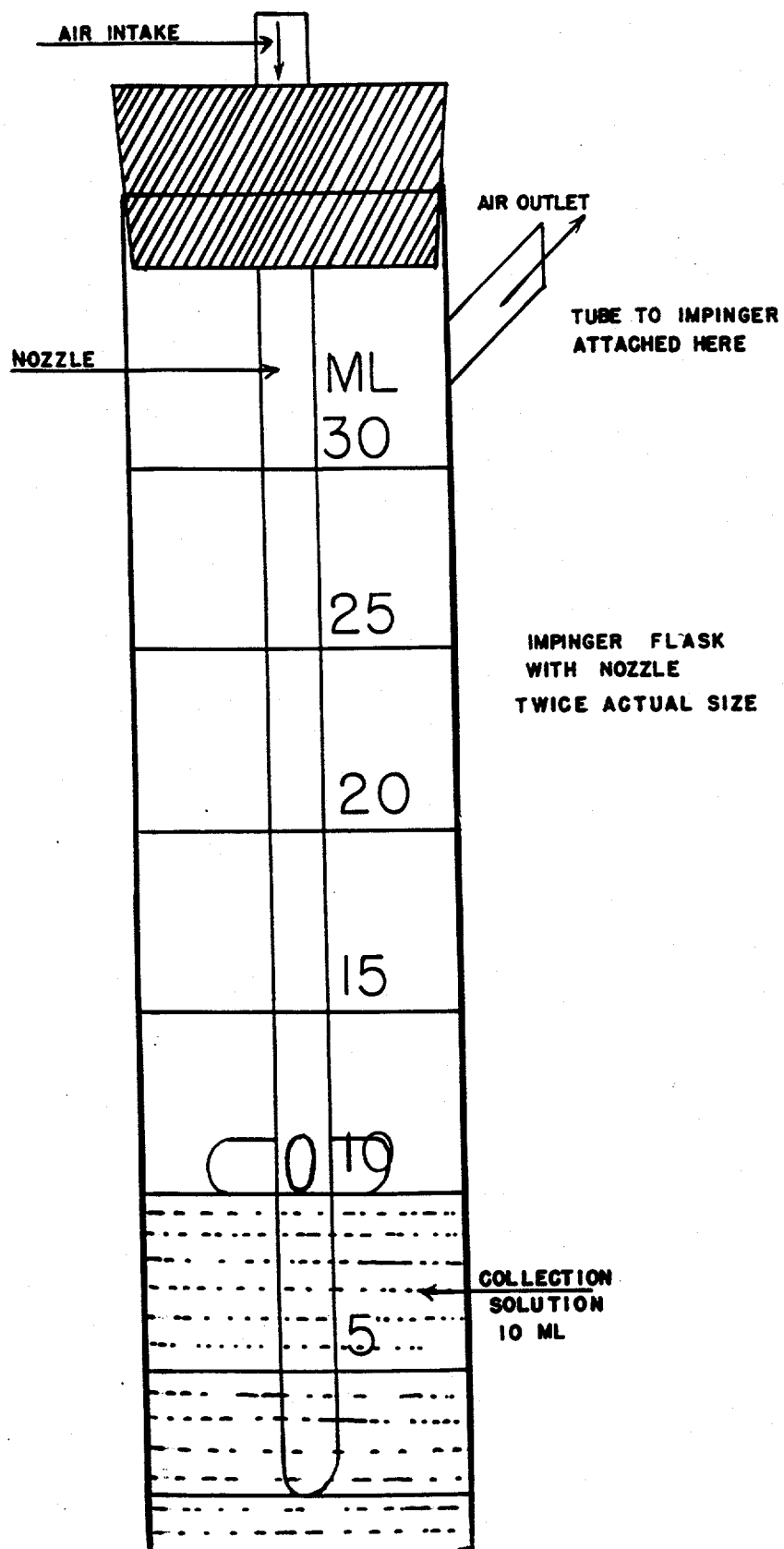
SAMPLING AND DETERMINATION OF MERCURY VAPOR

IN THE ATMOSPHERE

Method:

An atmosphere to be sampled for mercury vapor is drawn through an iodine-potassium iodide solution in a Midget Impinger flask. The analysis of the mercury collected in the iodine solution is made according to the colorimetric method of Polejaeff, modified slightly to meet K-25 requirements. This method is based upon the formation of increasingly intense colored precipitates resulting from the precipitation of mercury iodide on a white cuprous iodide matrix.

Reagents and Apparatus:

1. Iodine solution, 0.05 per cent - Dissolve 0.5 gram iodine and 6.0 grams potassium iodide in distilled water and dilute to a liter.

2. Copper sulfate solution, 10 per cent - Dissolve 15.6 grams cupric sulfate (five water of crystallization) in distilled water and dilute to 100 ml.

3. Sodium sulfate solution, 1 N.

4. Stock mercury standard solution (0.0712 milligrams of mercury per ml.) - Dissolve 0.0963 grams mercuric chloride in distilled water and dilute to a liter.

5. Working mercury standard solution - 1 ml. equivalent to 0.5 milligrams mercury per cubic meter air. Dilute 1 ml. of stock mercury to 10 ml. with distilled water.

6. M.S.A. Midget Impinger.

7. M.S.A. Midget Impinger flask, 30 ml., and nozzle

Procedure:

A. __Collection:__ (See Procedure 9.3).

1. Charge a 30 ml. midget impinger flask with 10 ml. of the 0.05 per cent iodine solution.

2. Draw air to be sampled through the solution. Under normal conditions a one cubic foot air sample is taken at a rate of 0.1 cubic foot per minute.

B. __Analysis:__

1. Set up a series of seven standard tubes as follows:

Standard Series of Mercury Tubes

Test Tube No.	Dilute Mercury Standard - ml.	Distilled Water ml.	Equivalent Milligrams Mercury/ cu. meter (5 ml. aliquot used)
1	0.00	1.00	0.00
2	0.10	0.90	0.05
3	0.20	0.80	0.10
4	0.40	0.60	0.20
5	0.60	0.40	0.30
6	0.80	0.20	0.40
7	1.00	0.00	0.50

2. Add 5.0 ml. of 0.05 per cent iodine solution to each of the above tubes.

3. Transfer a 5.0 ml.* aliquot sample from the collection flask to another test tube and add 1.0 ml. of distilled water.

___

* If an aliquot of less than 5.0 ml. is used, the volume should be brought up to 5.0 ml. with 0.05 per cent iodine solution. Then add 1.0 ml. of distilled water and proceed with steps No. 4, 5, and 6.

4. Add 0.4 ml. 1 M sodium sulfite to both the unknown and the standard tubes. Mix by shaking vigorously.

5. Add 0.2 ml. 10 per cent copper sulfate to both the unknown and the standard tubes. Shake vigorously until the last trace of green color has disappeared.

6. Compare the unknown tube with the standard tubes. Report to the nearest match. <u>Note:</u> The precipitate should be kept thoroughly dispersed during the comparison.

Calculations:

The standard tubes are so graduated that, when 1 cubic foot of air is sampled and a 5.0 ml. aliquot of the iodine is used, the milligrams of mercury per cubic meter is read directly from the standard tube matched.

If other than the above conditions are used, the concentration of mercury may be calculated from the following equation:

$$\frac{1}{A} \times \frac{5}{B} \times \frac{R}{1} = \text{milligrams mercury per cubic meter}$$

Where:

A = volume of air sampled in cubic feet.

B = aliquot of iodine solution analyzed, in ml.

R = equivalent milligrams mercury per cubic meter, as read from standard tube matched.

DETERMINATION OF FLUORIDES IN URINE

Method:

A urine sample is evaporated and ashed in a nickel crucible. The ash is transferred to a steam distillation apparatus (see Figure 1) and the fluorine is distilled as hydrogen fluoride. The fluorine in the distillate is determined using an adaptation of the standard thorium-alizarin sulfonate titration method.

Reagents and Apparatus:

1. Calcium oxide, analytical grade, low fluoride content.

2. Silver sulfate, analytical grade, low fluoride content.

3. Sulfuric acid solution - 50 per cent acid by volume is distilled water.

4. Sulfuric acid solution - 1 part acid in 1600 parts distilled water by volume.

5. Silver nitrate solution - approximately 0.1 M.

6. Barium chloride solution - approximately 0.1 M.

7. Barium chloride solution - approximately 0.01 M in approximately 0.001 N hydrochloric acid.

8. Phenolphthalein indicator, 1 per cent in 50:50 ethanol and distilled water.

9. Sodium hydroxide solution, 0.01 N.

10. Sodium alizarin sulfonate solution, 0.01 per cent in distilled water.

11. Hydrochloric acid solution - 0.04 N.

12. Thorium nitrate solution - 0.001 N.

13. Standard sodium fluoride solution - 10 micrograms fluoride per ml. solution.

14. Nickel crucibles, 75 ml. low form, with covers.

15. Hot plate with asbestos pad.

16. Muffle furnace.

17. Steam distillation apparatus. (See figure 1).

18. Micro-Bunsen and Meker burners.

19. 100 ml. Nessler tubes and illuminated tube rack.

20. Automatic micro burettes, 10 ml.

Procedure:

A. Evaporation and Ashing:

1. Wash the nickel crucible with warm 1:5 hydrochloric acid, and rinse
   well with tap water followed by distilled water.

2. Place 0.700 gm. calcium oxide in bottom of crucible.

3. Pipette 50 ml. urine into crucible in such a manner as to disperse
   the calcium oxide throughout.

4. Evaporate to complete dryness on hot plate covered with asbestos
   pad. This should take about four hours.

5. Ash in muffle furnace for forty-five minutes to one hour at 700° C.

6. Remove, cool, and scrape down sides and break up deposit to fine
   powder. Return to muffle furnace until uniform light gray ash is
   obtained.

B. Distillation:

1. Place 3.90 gm. silver sulfate in clean distillation flask.

2. Transfer the urine ash to the distillation flask, washing the
   crucible residue into the flask with two approximately ten ml.
   portions of distilled water.

3. Swirl contents of flask occasionally for five minutes.

4. Wash crucible with another ten ml. portion of distilled water and two ml. of 50 per cent sulfuric acid solution. Add this wash to the flask and immediately insert the still head and connect the condenser.

5. Add twenty ml. of 50 per cent sulfuric acid solution through the steam inlet tube and wash acid down with a few ml. of distilled water. Close off the steam inlet tube.

6. Heat the distillation flask with a micro Bunsen burner. Heat the steam generator with a Meker burner. When the contents of the flask reach 130° C. connect in the steam generator. Hold the flask temperaturne at 130° C. and distill at the rate of about one drop per second.

7. Collect 250 ml. of distillate.

   Note: Immediately after use, separate the still head from the flask and the condenser, otherwise the glass joints may freeze. Wash all three parts copiously with tap water followed by distilled water.

8. Test five ml. portions of the distillate with five drops of approximately 0.1 M barium chloride solution and with five drops of approximately 0.1 M silver nitrate. If either test gives a precipitate the distillate must be rejected.

C. Titration:

   Note: Several of the cations and anions present in the final solution titrated are known to influence the thorium alizarin lake. These interferences are present in balanced quantities, however, and accurate fluoride determination under these conditions has been verified experimentally.

1. Pipette 50 ml. of distillate into a 100 ml. Nessler tube. This tube is referred to as the "unknown".

Note: This aliquot will give satisfactory results for most urines. If high concentrations of fluoride are encountered, correspondingly smaller aliquots should be used so as to use between 2.0 and 4.0 ml. of standard sodium fluoride in the final step of the titration.

2. Pipette 50 ml. distilled water into a matching Nessler tube. This tube is referred to as the "blank".

3. Pipette 2 ml. of approximately 0.01 M barium chloride solution into both the "unknown" and "blank" tubes.

4. Titrate the "unknown" tube with 1/1600 sulfuric acid solution (drop by drop) until the first faint barium sulfate precipitate is observed.

5. Titrate the "blank" tube with 1/1600 sulfuric acid solution (drop by drop at same rate as in step No. 4) until the first faint barium sulfate precipitate is observed.

6. Add one drop of phenolphthalein indicator solution to both the "unknown" and "blank" tubes.

7. Very carefully titrate the "unknown" tube to a very faint pink color with 0.01 N sodium hydroxide.

8. Very carefully titrate the "blank" tube to a matched faint pink color with 0.01 N sodium hydroxide.

Note: During steps No. 4, 5, 7, and 8, particular care must be taken to avoid churning carbon dioxide from the air into the tubes.

9. Add 2 ml. of 0.01 per cent sodium alizarin sulfonate solution and 4 ml. of 0.04 N hydrochloric acid to both the "unknown" and "blank" tubes.

10. Titrate the "unknown" tube with 0.001 N thorium nitrate until a faint but definite pink color is obtained. Record the amount of thorium nitrate used and add the same amount to the "blank" tube.

11. Carefully titrate the "blank" tube with standard sodium fluoride (10 micrograms fluoride per ml.) until it exactly matches the color of the "unknown" tube. Record the amount of sodium fluoride used.

Calculation:

In order to calculate the final result, the "reagent blank" must be known. This is obtained by making several complete determinations as described above, except that 50 ml. of distilled water is run in place of the 50 ml. urine sample.

$$(U - R) \times \frac{10}{1000} \times \frac{A}{B} \times \frac{1000}{C} = \text{mg. fluoride per liter urine}$$

Where: factor $\frac{10}{1000}$ converts ml. sodium fluoride used to mg. fluoride

A is ml. distillate collected.

B is ml. aliquot of distillate titrated.

C is ml. urine sample taken for analysis.

U is ml. sodium fluoride solution to titrate urine sample.

R is ml. sodium fluoride solution to titrate "reagent blank" run.

DETERMINATION OF FLUORIDES
IN URINE
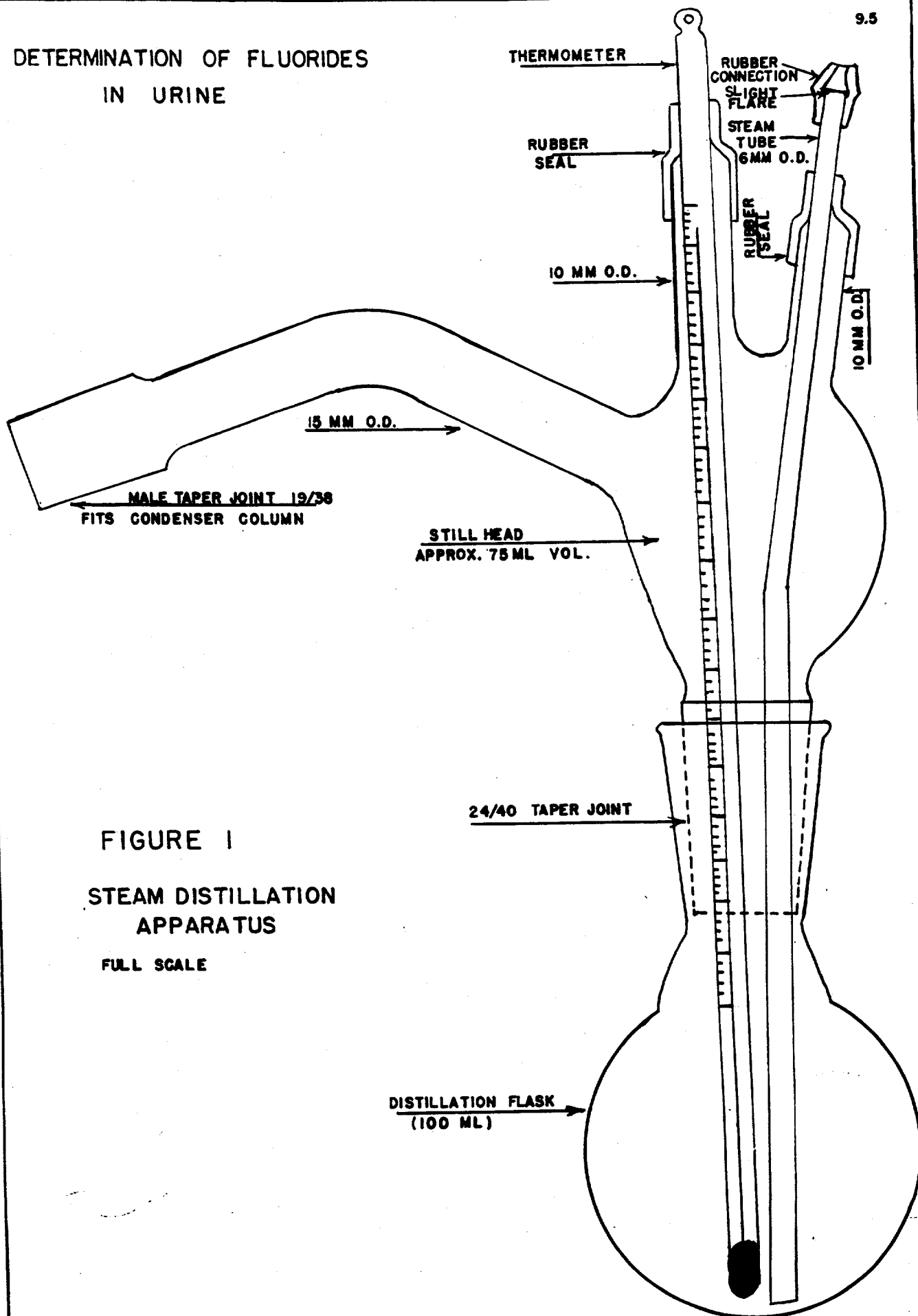
FIGURE I

STEAM DISTILLATION
APPARATUS

FULL SCALE

9.5

THERMOMETER

RUBBER
CONNECTION
SLIGHT
FLARE

STEAM
TUBE
6 MM O.D.

RUBBER
SEAL

RUBBER
SEAL

10 MM O.D.

10 MM O.D.

15 MM O.D.

MALE TAPER JOINT 19/38
FITS CONDENSER COLUMN

STILL HEAD
APPROX. 75 ML VOL.

24/40 TAPER JOINT

DISTILLATION FLASK
(100 ML)

THE COLLECTION AND DETERMINATION OF FLUORINE AND WATER

SOLUBLE FLUORIDES IN THE ATMOSPHERE

Method:

An air sample is collected in an evacuated bulb containing a dilute sodium
hydroxide solution. The fluoride is dissolved from the gas by means of the
alkaline solution, which in turn is titrated using an adaptation of the standard
thorium-alizarin sulfonate method for fluorides.

Reagents and Apparatus:

1. Sodium hydroxide solution - 0.1 N.

2. Sodium hydroxide solution, 0.01 N.

3. Sodium alizarin sulfonate solution (alizarin red S, certified) 0.01
    per cent in distilled water.

4. Hydrochloric acid solution, 0.04 N.

5. Thorium nitrate solution, 0.001 N.

6. Standard sodium fluoride solution, 10 micrograms fluoride ion per ml.
    solution.

7. Collection bulb, (see Figure 1).

8. Nessler tubes, 100 ml.

Procedure:

A. Preparation of the collection bulb:

1. Rinse the bulb and stopper containing the stopcock four times by
    filling with tap water and shaking vigorously. Repeat using four
    rinses of distilled water.

2. Pour 250 ml. of distilled water and 5 ml. of 0.1 N sodium hydroxide
    into the bulb.

3. Tightly stopper the bulb and evacuate through the stopcock for 5
    minutes with a high vacuum oil pump. Use a cold trap between the bulb
    and the pump.

B. __Collection of the sample:__

1. Withdraw the stopper from the bulb and hold it well away from the mouth of the bulb for several seconds.

2. Replace the stopper and __immediately__ shake vigorously a few times.

3. Make certain the stopper is tight and the stopcock closed.

4. Shake 300 times by moving the bulb up and down energetically through a vertical distance of nine inches. If done sufficiently energetically this should require approximately two minutes.

5. If the sample is not to be titrated immediately, transfer the sample from the bulb to a suitable clean glass-stoppered bottle and clearly label.

6. Thoroughly rinse the bulb immediately with tap water and distilled water as described above and return it to its storage container.

C. __Analysis of the sample:__

1. Pipette a 100 ml. aliquot of the sample into a clean 100 ml. Nessler tube. This tube is referred to as the "sample".

2. To a second Nessler tube, add 2 ml. of 0.1 N sodium hydroxide and distilled water up to the 100 milliliter mark. This tube is referred to as the "blank".

3. Add 2 ml. of 0.01 per cent sodium alizarin sulfonate to both the sample and the blank.

4. Add 6.0 ml. of 0.04 N hydrochloric acid to both the sample and the blank.

5. Back titrate both the sample and the blank with 0.01 N sodium hydroxide to matched, very light pink, end point of alizarin. (The alizarin merely acts as a pH indicator in this step.)

6. Add 4 ml. of 0.04 N hydrochloric acid to both the sample and the blank.

7. Titrate the <u>sample</u> with 0.001 N thorium nitrate to a faint, but definite, pink color. Record this volume and add the same volume of thorium nitrate to the blank.

8. Back titrate the <u>blank</u> with standard sodium fluoride to match the pink color of the sample.

   When the two tubes appear almost matched, add the standard sodium fluoride to the blank in 0.01 ml. portions. Make a temporary recording of each portion used. The actual end point is the matched color which can be unmatched by the addition of another 0.01 ml. portion of standard sodium fluoride.

   <u>Note:</u> In matching the pink colors, some difference between the background shades of the sample and blank may be noted. Thus the matched pink colors may be of slightly different shades, but should match in intensity.

<u>Calculation:</u>

$$\frac{M}{W} \times A \times B \times \frac{C}{D} \times \frac{1}{E} \times 1,000,000 = \text{p.p.m. fluoride, by volume, in air.}$$

Where:

   M = mole volume in liters corrected to existing conditions.

   W = gram molecular weight of fluoride.

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A = volume in ml. of sodium fluoride used to titrate blank.

B = fluoride equivalent of standard sodium fluoride solution

C = ml. dilute sodium hydroxide solution in the collection bulb.

D = volume in ml. of aliquot titrated.

E = volume of collection bulb in liters.

THE COLLECTION AND DETERMINATION
OF FLUORINE AND WATER SOLUBLE
FLUORIDES IN THE ATMOSPHERE

STOPCOCK

RUBBER
STOPPER

FIVE LITER BULB
(TAPED)
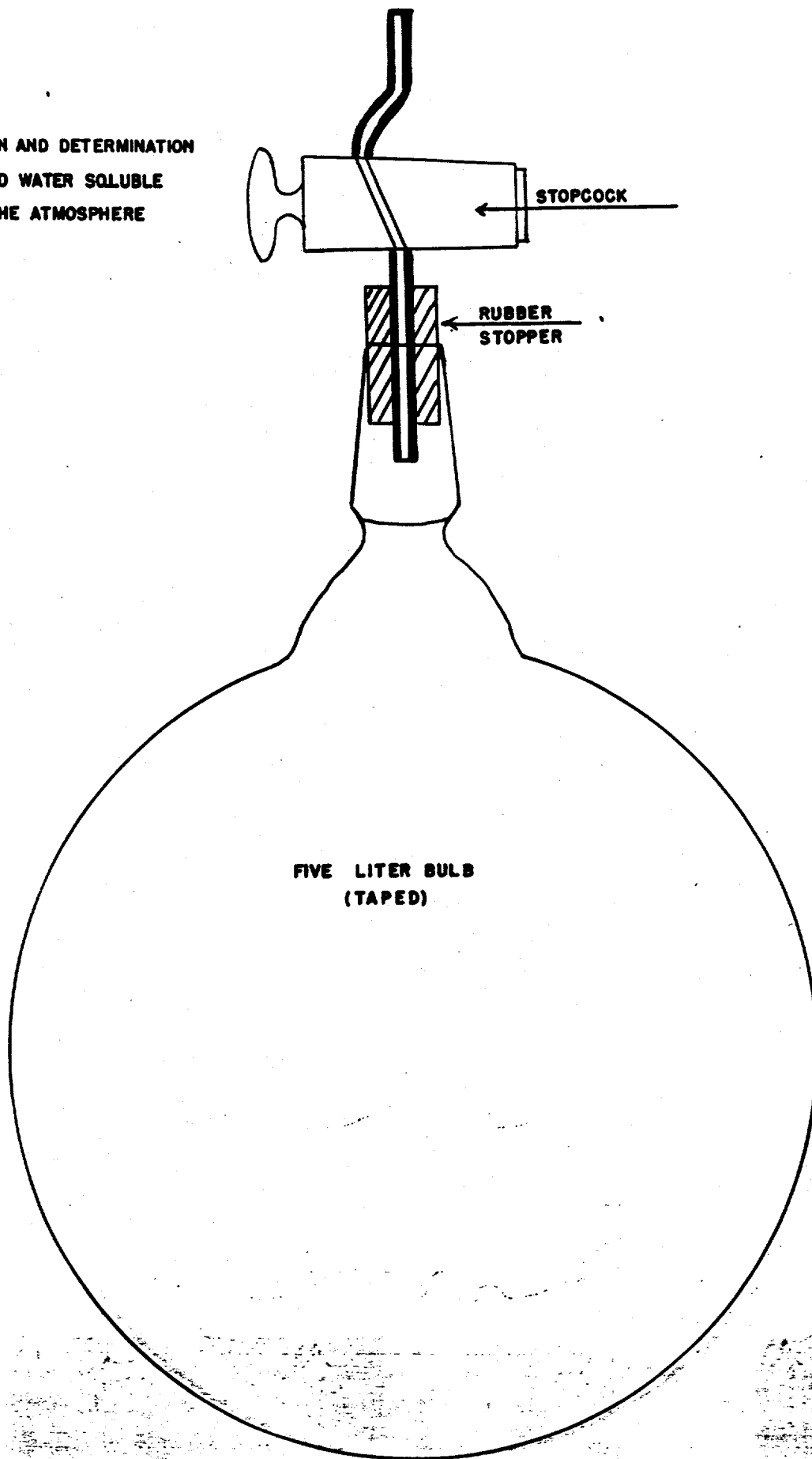
DETERMINATION OF TRICHLOROETHYLENE IN THE ATMOSPHERE

BY USE OF THE IMPERIAL HALIDE GAS LEAK DETECTOR

Method:

Flame colors produced by the Imperial Halide Leak Detector give a semi-quantitative evaluation of the concentration of trichloroethylene in the atmosphere. The flame color is due to volatile copper halides.

Reagents and Apparatus:

1. Imperial Halide Gas Leak Detector.

2. Small Prest-O-Lite cylinder.

Procedure:

A. Lighting the burner:

1. Open the tank valve about one-third to one-half turn.

2. Crack open the shut-off valve on the torch handle.

3. Light the burner through the side opening of the flame shield.

4. Adjust the flame so that the tip of the inner cone is level with the copper reaction plate.

Note: Much of the difficulty encountered in lighting the burner, may be prevented by closing off the rubber probe tube during the lighting and initial adjustments.

B. Determining the trichloroethylene concentration:

1. Allow the detector to burn until the copper reaction plate is clean. A characteristic "hot" blue flame should be obtained.

2. Probe the area to be tested with the rubber tube attached to the air mixer assembly.

3. Determine the concentration of trichloroethylene in the air by comparing the flame color with the following table:

Trichloroethylene in the Atmosphere

P.p.m. by volume	Inside Cone	Outside Cone	Tip of flame
Less than 75	"Hot" blue	"Hot" blue	"Hot" blue
100- 200	"Hot" blue	"Hot" blue	Green
300- 500	Green	Green	Aquamarine
600- 800	Aquamarine	Aquamarine	Aquamarine
900-1000	Aquamarine	Aquamarine	Purple
1500	Aquamarine	Purple	Orange
2000 & over	Aquamarine	Purple	Orange

(Smoke produced)

-1-

SAFETY SAMPLE FOR C-216

Add a few drops starch solution to test tube one half full of KI solution. Attach apparatus to sample line. Furnace pressure must be 16 lbs. or more before admitting sample. Proceed with analysis by slowly bubbling gas through KI solution in test tube. If solution remains colorless no C-216 is present. If no C-216 is detected record data, and inform operator on special yellow safety sample form that it is safe to remove converter. If C-216 is present, record data and inform operator with written report of presence of C-216. He will have to purge with G-74. Retest.

Note: Negative reports for safety samples are to be made upon yellow safety sample report forms only.

Positive reports for safety samples are to be made on regular white slips. Write word "Positive" in space opposite "Percent C-216".

Reconditioned Furnace:

Run analysis according to regular procedure and in addition complete on each analysis the C-216, O_2 and HF. Do not report O_2 and HF data to area.

Re-exposure:

Run analysis as per schedule except do not complete analysis for HF or O_2.

-1-

C-616 SAFETY SAMPLING ON STAND AND UNITS

When sampling for C-616 on a unit, have pressure at 13# psia. Attach rubber tube to male sampling joint. If no sampling joint is connected, use the copper tube that the male joint is usually attached to. Attach salicyclic acid tube to end of rubber tube and open C-18 valve. (Note: If sufficient pressure is not attainable connect vacuum line to one end of the salicylic acid tube and pull gas through). If the salicylic acid crystals turn brown immediately, C-616 is present and unit must be evacuated. Then repeat the preceding steps. (Note: After several consecutive positive samples take steps to have unit heated and evacuated). If salicylic acid crystals remain white the sample is negative.

In case a sample is wanted at different points on the furnace, such as on connection where C-616 sampling buggy is attahced, remove connection to buggy and connect salicylic acid tube to line. Ir pressure is not sufficiently high here, use a vacuum pump to pull sample through tube.

SAFETY SAMPLE FOR C-616 ON STOKES PUMP

Pressure in unit should be 18# psia. When 18# psia is reached, have Stokes pump shut off and discharge valve closed. Insert rubber stopper having short length of 3/8" copper tubing through it into refilling cap in Stokes pump case. Connect rubber tube with salicylic acid tube attached to 3/8" copper tubing and pull sample through with a vacuum pump. (Note: The temperature of the Stokes pump is $140^{\circ}F$ and the oil temperature is $100^{\circ}F$. This is sufficient to remove C-616 when purged with G-74.